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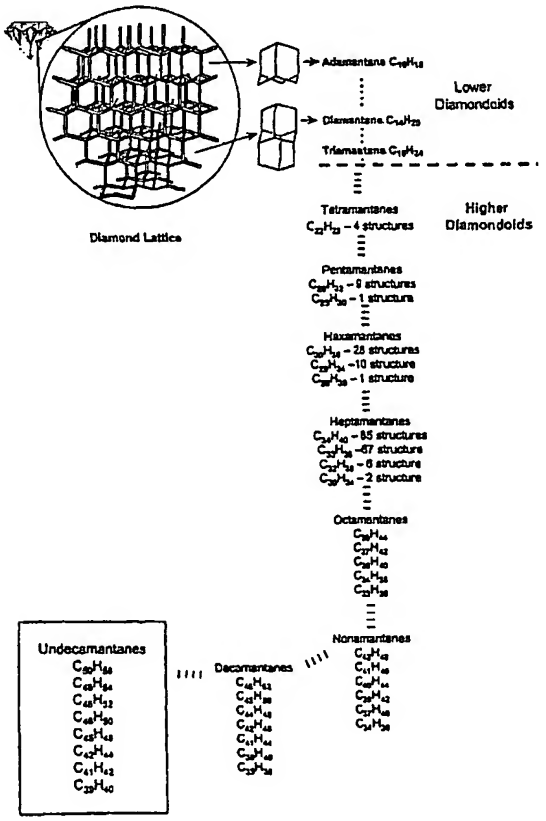
(54) Title: COMPOSITIONS COMPRISING HIGHER DIAMONDOIDS AND PROCESSES FOR THEIR SEPARATION



(57) Abstract: Higher diamondoids ranging from tetramantanes through undecamantanes are disclosed in isolated and enriched forms. Methods for obtaining these higher diamondoids are disclosed, as well.

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COMPOSITIONS COMPRISING HIGHER DIAMONDOIDS AND PROCESSES FOR THEIR SEPARATION

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] This invention is directed to isolated or enriched higher diamondoid components and to compositions comprising one or more higher diamondoid components. This invention is also directed to novel methods for the separation and isolation of higher diamondoid components into recoverable fractions from a feedstock containing one or more higher diamondoid components.

References

[0002] The following publications and patents are cited in this application as superscript numbers:

[0003] [1] Fort, Jr., et al., Adamantane: Consequences of the Diamondoid Structure, Chem. Rev., :277-300 (1964)

[0004] [2] Sandia National Laboratories (2000), *World's First Diamond Micromachines Created at Sandia,* Press Release, (2/22/2000) www.Sandia.gov.

[0005] [3] Lin, et al., *Natural Occurrence of Tetramantane ($C_{22}H_{28}$),Pentamantane ($C_{26}H_{32}$) and Hexamantane ($C_{30}H_{36}$) in a Deep Petroleum Reservoir,* Fuel, (10):1512-1521 (1995)

[0006] [4] Chen, et al., *Isolation of High Purity Diamondoid Fractions and Components,* U.S. Patent No. 5,414,189, issued May 9, 1995

[0007] [5] Alexander, et al., *Removal of Diamondoid Compounds from* Hydrocarbonaceous *Fractions,* U.S. Patent No. 4,952,747, issued August 28, 1990

[0008] [6] Alexander, et al., Purification *of Hydrocarbonaceous Fractions,* U.S. Patent No. 4,952,748, issued August 28, 1990

[0009] [7] Alexander, et al., Removal *of Diamondoid Compounds from Hydrocarbonaceous Fractions,* U.S. Patent No. 4,952,749, issued August 28, 1990

[00010] [8] Alexander, et al., *Purification of Hydrocarbonaceous Fractions,* U.S. Patent No. 4,982,049, issued January 1, 1991

[00011] [9] Swanson, Method *for Diamondoid Extraction Using a Solvent System,* U.S. Patent No. 5,461,184, issued October 24, 1995

[00012] [10] Partridge, et al., *Shape*-Selective *Process for Concentrating Diamondoid-Containing* Hydrocarbon *Solvents,* U.S. Patent No. 5,019,665, issued May 28, 1991

[00013] [11] Dahl, et al., Diamondoid *Hydrocarbons as Indicators of Natural Oil Cracking,* Nature, , 54-57 (1999).

[00014] [12] McKervey, Synthetic *Approaches to Large Diamondoid Hydrocarbons,* Tetrahedron, 971-992 (1980).

[00015] [13] Wu, et al., *High* Viscosity *Index Lubricant Fluid,* U.S. Patent No. 5,306,851, issued April 26, 1994.

[00016] [14] Chung et al., Recent *Development in High-Energy Density Liquid Fuels,* Energy and Fuels, 641-649 (1999).

[00017] [15] Balaban et al., *Systematic Classification and Nomenclature of Diamond Hydrocarbons-1, Tetrahedron,* 34,3599-3609.

[00018] All of the above publications and patents are herein incorporated by reference in their entirety to the same extent as if each individual publication or patent was specifically and individually indicated to be incorporated by reference in its entirety.

[00019] Diamondoids are hydrocarbon molecules possessing amazingly rigid structures that contain carbon atom frameworks that are superimposable on the diamond crystal lattice[1] (see FIG. 1). Adamantane, a ten-carbon molecule, is the smallest member of the diamondoid series, consisting of one cage-shaped diamond crystal subunit. Adamantane is commercially available and is widely used as a chemical intermediate. It can be synthesized and it can be recovered from petroleum. Diamantane contains two face-fused diamond subunits and triamantane three. These three materials have been synthesized and isolated from petroleum and have received research attention. Adamantane, diamantane and triamantane are classified as "lower diamondoids". Tetramantane, pentamantanes, etc., have characteristics (including multiple isomers, chirality and, above tetramantane, multiple molecular weight forms) that differ from the lower diamondoids, and are classified as "higher diamondoids". While only one of the higher diamondoids has been synthesized, ideas concerning their structures and hypothetical properties have been set forth.

[00020] While adamantane, diamantane and triamantane show no isomers, it is understood that there should be four different isomeric tetramantanes; four different shapes containing four diamond-cage subunits that can be superimposed on the diamond crystal lattice in different ways. Two of these isomers are enantiomers (mirror images of each other). Because the four tetramantanes each have ten faces to which the next diamond-cage

unit could fuse, the number of pentamantanes increases over that of the tetramantanes. The number of possible isomers increases rapidly with each higher member of the diamondoid series. Also, because diamondoid crystal units can share more than a single face in some higher diamondoids, hydrogen to carbon ratios, i.e., the degree of condensation, also shows increasing variation, resulting in an increasing variety of molecular weights for each successive higher diamondoid family (FIG. 1). FIG. 2 is a table showing the different series of molecular weights calculated for higher diamondoids ranging from the tetramantanes to the undecamantanes.

[00021] Lower diamondoids are present in virtually every petroleum (oils and gas condensates) as well as oil source-rock extracts.[11] The natural concentration of diamondoids in petroleum varies by orders of magnitude. For instance, methyldiamantane concentrations in relatively low-maturity crude oils from the central valley of California, are on the order of a few parts per million (ppm). Low-maturity oils sourced from the Jurassic-age Smackover Formation, Gulf Coast, USA, have methyldiamantane concentrations of 20-30 ppm. Because diamondoids show much greater stabilities than other petroleum hydrocarbons, deeply-buried petroleums, which have undergone substantial cracking as a result of intense heat may have methyldiamantane concentration in the thousands of ppms. It is not understood how higher diamondoids could be formed in natural systems, but it may involve a process requiring millions of years.

[00022] The higher diamondoids, which include the tetramantanes, pentamantanes, etc., have received comparatively little attention. In fact, prior to the work of inventors Dahl and Carlson embodied in United States Patent Application Serial No. 60/262,842 filed January 19, 2001 and numerous subsequent filings, these compounds were hypothetical with only one such compound having been synthesized and a few others tentatively identified (but not isolated). More specifically, McKervey, *et al.* reported the synthesis of *anti*-tetramantane in low yields using a laborious, multistep process.[12] Higher diamondoids cannot be synthesized by carbocation isomerization methods useful for the lower diamondoids. Lin, *et al.* have suggested the existence of tetramantane, pentamantane and hexamantane in deep petroleum reservoirs from mass spectroscopy alone and without any attempt to isolate materials.[3] The possible presence of tetramantane and pentamantane in pot material recovered after a distillation of a diamondoid-containing feedstock has been discussed by Chen, *et al.*[4] Again, they made no attempt to isolate materials from this pot material.

[00023] As additional background, it is pointed out that the present inventors separately isolated the higher diamondoid cyclohexamantane, the most condensed member of the hexamantane series, and have made that invention the subject of its own patent application.

[00024] To summarize, the higher diamondoids have not been identified or isolated or otherwise provided with the following exceptions: *iso*-tetramantane – synthesized[12] and unsubstituted cyclohexamantane – separately discovered by the present inventors.

SUMMARY OF THE INVENTION

[00025] This invention provides higher diamondoids, as enriched or isolated compounds. It also provides the individual higher diamondoid isomers (referred to as "higher diamondoid components" as enriched or isolated compounds for the first time. In addition, this invention provides processes with which the enriched and isolated higher diamondoids and higher diamondoid components can be obtained.

[00026] In accord with this invention we have isolated as crystals a variety of previously unavailable higher diamondoids including tetramantanes, pentamantanes, hexamantanes, heptamantanes, octamantanes, nonamantanes and even decamantane. The isolation of the higher molecular weight higher diamondoids is especially unexpected in light of our finding that the relative abundance of each diamondoid family (tetra vs. penta, etc.) drops by a factor of about 10 for each crystal sub-unit added to the structure. This means that the decamantane we have isolated, for example is about 10^{-6} times as prevalent in feedstocks as any of the tetramantanes, including the species which was synthesized in the prior art.

BRIEF DESCRIPTION OF THE DRAWINGS

[00027] FIG. 1 illustrates the cage-shaped structure of diamondoids and their correlation to diamonds. Specifically illustrated is the correlation of the structures of diamondoids to subunits of the diamond crystal lattice.

[00028] FIG. 2 is a table depicting the different molecular weights shown by each higher diamondoid series.

[00029] FIG. 3 illustrates the structure of the tetramantanes provided by this invention.

[00030] FIG. 4 illustrates that the four tetramantanes have carbon frameworks that correlate with the diamond lattice and can be viewed into their 100 lattice plane (FIG. 4A), 110 lattice plane (FIG. 4B) and 111 diamond lattice plane (FIG. 4C).

[00031] FIG. 5 illustrates the structure of the pentamantanes provided by this invention.

[00032] FIG's. 6A, 6B, 6C and 6D illustrate the structure of the hexamantanes provided by this invention.

[00033] FIG's. 7A, 7B and 7C illustrate the structure of the heptamantanes provided by this invention. Only one of each enantiomer is shown.

[00034] FIG. 8 illustrates the structure of the octamantanes provided by this invention. Only examples of the 500, 486, 472 and 432 molecular weight forms are shown.

[00035] FIG. 9 illustrates the structure of the nonamantanes provided by this invention. Only examples of each molecular weight family are shown.

[00036] FIG. 10 illustrates the structure of the decamantanes provided by this invention. Only examples of each molecular weight family are shown.

[00037] FIG. 11 illustrates the structure of the undecamantanes provided by this invention. Only examples of each molecular weight family are shown.

[00038] FIG. 12 gives a flow chart representing the various steps used in the isolation of higher diamondoid-containing fractions and individual higher diamondoid components. Note that the steps can in some cases be used in a different sequence and possibly skipped as discussed in the Examples.

[00039] FIG's. 13A and 13B are compilations of the GC/MS and HPLC properties of various higher diamondoids included in this application.

[00040] FIG. 14 shows the two-HPLC column strategy used to isolate individual tetramantanes and pentamantanes.

[00041] FIG. 15 illustrates the size and shape of selected higher diamondoids relative to C_{60} (Buckminsterfullerene) and a representative carbon nanotube used in the development of molecular electronic devices. The carbon framework structures of the selected diamondoids can be found in FIG's 5, 6, 8, 9 and 10.

[00042] FIG. 16 illustrates the gas chromatogram of a gas condensate feedstock; one of the original feedstocks used in the Examples (Feedstock A); showing minute concentrations of higher diamonds (not detectable on this scale).

[00043] FIG. 17 illustrates a high temperature simulated distillation profile of Feedstock B using the atmospheric distillation 650 °F + bottoms as feedstock. This figure also illustrates the targeted cut points (1-10) we used for higher diamondoid isolations.

[00044] FIG's. 18A and 18B illustrate gas chromatograms (FID) of distillate fraction #6 (Table 3B, FIG. 18) of Feedstock B 650 °F + distillation bottoms, and the resulting product of pyrolytic processing. These figures show that nondiamondoid components have been destroyed by the pyrolytic processing and that higher diamondoids, especially hexamantanes, have been concentrated and made available for isolation.

[00045] FIG's. 19 and 20 are charts illustrating elution sequences for a variety of individual higher diamondoids (hexamantanes) on two different HPLC chromatography columns: ODS and Hypercarb as discussed in Examples 1 and 7.

[00046] FIG's. 21A and 21B illustrate the preparative capillary gas chromatographic data for tetramantane isolations carried out in Examples 3 and 5. FIG. 21A shows cuts made on distillate fraction #33, Feedstock A. The bold face numbers refer to peaks of the tetramantanes. FIG. 21B shows peaks isolated and sent to the traps. The circled numbered peaks (2, 4, and 6) are the tetramantanes. It is noted that both enantiomers of the optically-active tetramantane are contained within one of these peaks.

[00047] FIG's. 22A, 22B and 22C illustrate photomicrographs of tetramantane crystals isolated from Feedstock A by preparative gas chromatography (FIG. 21). FIG. 22A was isolated from trap fraction #2, FIG. 22B was isolated from trap fraction #4, and FIG. 22C was isolated from trap fraction #6. Because the two enantiomeric tetramantanes have identical GC retentions times in FIG. 21, one of the crystals contains both enantiomers.

[00048] FIG. 23A illustrates the gas chromatogram of Feedstock B atmospheric distillation hold up fraction, exemplified in Example 1, which was used as feedstock in pyrolytic processing. The hold up fraction is the material recovered from the distillation column after distillation of Feedstock B at approximately 650°F. Tetramantanes #1 to #3 are shown.

[00049] FIG. 23B illustrates the gas chromatogram of the pyrolytic product from the starting material in FIG. 23A, i.e. the holdup fraction of Feedstock B atmospheric distillation 650 °F + bottoms, showing the degradation of non-diamondoid components.

[00050] FIG.'s 24A and 24B compare the gas chromatograms of a tetramantane-containing starting mixture injected into a Vydac ODS HPLC column, and HPLC cut #6 enriched in a tetramantane component.

[00051] FIG. 25 illustrates a preparative ODS HPLC isolation of the holdup fraction of Feedstock B atmospheric distillation 650 °F + bottoms, showing fractions taken at various retention times and the elution order of the tetramantane components and the location time of fraction #12 used in subsequent isolations steps. FIG. 23 above, displays the gas chromatograph of this feedstock.

[00052] FIG. 26 illustrates the HPLC chromatogram of fraction 12 (FIG. 25) run on Hypercarb stationary phase with acetone mobile phase resulting in the isolation of tetramantane #2.

[00053] FIG's. 27A and 27B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of tetramantane #1 isolated by using two different HPLC columns.

[00054] FIG's. 28A and 28B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of tetramantane #2 isolated by using two different HPLC columns.

[00055] FIG's. 29A and 29B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of tetramantane #3 isolated by using two different HPLC columns.

[00056] FIG's. 30A and 30B show the GC/MS total ion chromatogram (TIC) and mass spectrum of a methyltetramantane isolated using Hypercarb HPLC.

[00057] FIG's. 31A and 31B illustrate a preparative capillary gas chromatographic data for pentamantane isolations. FIG. 31A, shows the first column cut containing one of the pentamantanes from thermally treated Feedstock B. The material in that cut was separated on a second column. FIG. 31B, shows the second column peak sent to the trap. Pentamantane #1, the first pentamantane to elute in GC/MS analysis, was isolated in trap 6.

[00058] FIG's. 32A and 32B show the GC/MS total ion chromatogram and mass spectrum of pentamantane #1 isolated by preparative capillary gas chromatography.

[00059] FIG. 33A is a photomicrograph of pentamantane #1 crystals isolated from Feedstock B by preparative gas chromatography (FIG. 31 and 32). FIG. 33B illustrates a pentamantane co-crystal.

[00060] FIG. 34 illustrates the preparative HPLC Refractive Index trace (with negative polarity) of Feedstock B distillate cut pyrolysis product saturated hydrocarbon fraction showing HPLC fractions taken using octadecyl silane columns and acetone mobile phase. Pentamantanes are numbered in order of their elution on the GC/MS analyses.

[00061] FIG. 35 illustrates the chromatogram of ODS HPLC fraction 11 (FIG. 34) run on Hypercarb stationary phase with acetone mobile phase resulting in the isolation of pentamantane #1.

[00062] FIG's. 36A and 36B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of pentamantane #1 isolated using two different HPLC columns.

[00063] FIG's. 37A and 37B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of pentamantane #2 isolated using two different HPLC columns.

[00064] FIG's. 38A and 38B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of pentamantane #3 isolated using two different HPLC columns.

[00065] FIG's. 39A and 39B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of pentamantane #4 isolated using two different HPLC columns.

[00066] FIG's. 40A and 40B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of pentamantane #5 isolated using two different HPLC columns.

[00067] FIG's. 41A and 41B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of pentamantane #6 isolated using two different HPLC columns.

[00068] FIG's. 42A and 42B illustrate the preparative capillary gas chromatographic data for hexamantane isolations. FIG. 42A, shows the first column cuts containing two of the hexamantanes from Feedstock B. FIG. 42B, shows the second column peaks isolated and sent to the traps. From this procedure pure hexamantanes were isolated (FIG.'s 43 and 44), hexamantane #2, the second hexamantane to elute in our GC/MS assay, while hexamantane #8 is the eighth to elute.

[00069] FIG's. 43A and 43B illustrate the GC/MS total ion chromatogram and mass spectrum of a hexamantane #2 isolated by preparative capillary gas chromatography.

[00070] FIG's. 44A and 44B illustrate the GC/MS total ion chromatogram and mass spectrum of a hexamantane #8 highly concentrated by preparative capillary gas chromatography. A minor amount of a methylheptamantane (408 molecular weight) is present in this sample.

[00071] FIG. 45 illustrates a photomicrograph of hexamantane #2 crystals isolated from Feedstock B by preparative gas chromatography (FIG. 42 and 44).

[00072] FIG. 46 illustrates a photomicrograph of hexamantane #8 crystals isolated from Feedstock B by preparative gas chromatography (FIG. 145 and 147).

[00073] FIG's. 47A and 47B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of hexamantane #8 in ODS HPLC fraction #39.

[00074] FIG's. 48A and 48B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of hexamantane #10 in ODS HPLC fraction #48.

[00075] FIG's. 49A and 49B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of hexamantane #6 in ODS HPLC fraction #63.

[00076] FIG's. 50A and 50B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of hexamantane # 2 greatly enriched in Hypercarb HPLC fraction #53.

[00077] FIG's. 51A and 51B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of hexamantane # 13 isolated using two different HPLC columns.

[00078] FIG's. 52A and 52B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of hexamantane # 7 isolated using two different HPLC columns.

[00079] FIG's. 53A and 53B illustrate GC/MS reconstructed ion chromatogram m/z 382 and mass spectrum of a condensed "irregular" hexamantane (mol. wt. 382) in the saturated hydrocarbon fraction of the product of the pyrolytic processing of Feedstock B distillation fraction #6.

[00080] FIG's. 54A and 54B illustrate GC/MS reconstructed ion chromatogram m/z 382 and mass spectrum of an irregular hexamantane (mol. wt. 382) in the ODS HPLC fraction #36.

[00081] FIG's. 55A and 55B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of a methylhexamantane (mol. wt. 410) isolated in ODS HPLC fraction #55.

[00082] FIG. 56 illustrates GC/MS total ion chromatogram (TIC) of cyclohexamantane and methylcyclohexamantane-containing ODS HPLC combined fractions #23-26.

[00083] FIG's. 57A and 57B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of a methylcyclohexamantane #1 (mol. wt. 356) isolated using multi-column stationary phase HPLC (ODS followed by Hypercarb).

[00084] FIG's. 58A and 58B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of a methylcyclohexamantane #2 (mol. wt. 356) isolated in high purity using multi-column stationary phase HPLC (ODS followed by Hypercarb).

[00085] FIG's. 59 and 60 show photomicrographs of crystals of methylcyclohexamantane #1 and methylcyclohexamantane #2 isolated using two different HPLC columns.

[00086] FIG's. 61A and 61B illustrate the preparative capillary gas chromatographic data for heptamantane isolations. FIG. 61A, shows the first column cuts containing two of the

heptamantanes from Feedstock B. FIG. 61B, shows the second column peaks isolated and sent to the traps. From this procedure pure heptamantane components were isolated (FIG 8 and 9) , heptamantane #1, the first heptamantane to elute in our GC/MS assay, and heptamantane #2 which is the second to elute.

[00087] FIG's. 62A and 62B illustrate the GC/MS total ion chromatogram and mass spectrum of a heptamantane #1 isolated by preparative capillary gas chromatography.

[00088] FIG's. 63A and 63B illustrate the GC/MS total ion chromatogram and mass spectrum of a heptamantane #2 highly concentrated by preparative capillary gas chromatography.

[00089] FIG. 64 illustrates photomicrographs of heptamantane #1 crystals isolated from Feedstock B by preparative gas chromatography (FIG's. 61 and 62).

[00090] FIG. 65 illustrates a photomicrograph of heptamantane #2 crystals isolated from Feedstock B by preparative gas chromatography (FIG's. 61 and 63).

[00091] FIG's. 66A and 66B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of heptamantane component #1 in ODS HPLC fraction #45.

[00092] FIG's. 67A and 67B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of heptamantane component #2 in ODS HPLC fraction #41.

[00093] FIG's. 68A and 68B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of heptamantane component #9 in ODS HPLC fraction #61.

[00094] FIG's. 69A and 69B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of heptamantane component #10 in ODS HPLC fraction #87.

[00095] FIG's. 70A and 70B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of heptamantane # 1 greatly enriched in Hypercarb HPLC fraction #55.

[00096] FIG's. 71A and 71B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of heptamantane #2 isolated using two different HPLC columns. Heptamantane #2 was isolated from ODS HPLC fraction #41 (FIG. 67) using the Hypercarb HPLC system.

[00097] FIG. 72 illustrates GC/MS reconstructed ion chromatogram m/z 420 showing a partially condensed heptamantane component (mol. wt. 420) in the ODS HPLC fraction #61.

[00098] FIG. 73 illustrates the mass spectrum of the molecular weight 420 heptamantane in FIG. 72.

[00099] FIG's. 74A and 74B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of a methylheptamantane component (mol. wt. 408) isolated in ODS HPLC fraction #51.

[000100] FIG's. 75A and 75B illustrate the GC/MS total ion chromatogram and mass spectrum of octamantane #1 highly concentrated by high performance liquid chromatography.

[000101] FIG. 76 illustrates a photomicrograph of octamantane #1 crystals isolated from Feedstock B by high performance liquid chromatography.

[000102] FIG's. 77A and 77B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of co-crystalline octamantane #3 and octamantane #5 (FIG. 78) grown from ODS HPLC fraction #63.

[000103] FIG's. 78A and 78B illustrate photomicrographs of co-crystalline octamantane #3 and #5, crystal B was dissolved in cyclohexane and analyzed by GC/MS (FIG. 77).

[000104] FIG's. 79A and 79B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of octamantane #1 and octamantane #10 containing ODS HPLC fraction #80.

[000105] FIG's. 80A and 80B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of an octamantane (molecular weight 500)-containing ODS HPLC fraction #92.

[000106] FIG's. 81A and 81B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of a methyloctamantane (mol. wt. 460) in ODS HPLC fraction #94.

[000107] FIG's. 82A and 82B illustrate the GC/MS total ion chromatogram and mass spectrum of a nonamantane concentrated by high performance liquid chromatography.

[000108] FIG's. 83A and 83B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of a nonamantane concentrated using two different HPLC columns.

[000109] FIG's. 84A and 84B illustrate a photomicrograph of a nonamantane crystal and a mass spectra of the dissolved crystal.

[000110] FIG's. 85A and 85B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of a methylnonamantane (mol. wt. 512).

[000111] FIG's. 86A and 86B illustrate the GC/MS total ion chromatogram and mass spectrum of [1231241(2)3], molecular weight 456, decamantane concentrated by high performance liquid chromatography.

[000112] FIG's. 87A and 87B illustrate GC/MS total ion chromatogram (TIC) and mass spectrum of [1231241(2)3], molecular weight 456, decamantane isolated using two different HPLC columns.

[000113] FIG's. 88A and 88B illustrate a photomicrograph of [1231241(2)3], molecular weight 456, decamantane crystal and a mass spectra of the dissolved crystal.

[000114] FIG's. 89A and 89B illustrate GC/MS selected ion chromatogram (TIC) and mass spectrum of a decamantane (mol. wt. 496).

[000115] FIG's. 90A and 90B illustrate GC/MS total ion chromatogram (TIC) of two methyldecamantanes (mol. wt. 470), and the mass spectrum of the one eluting at 18.84 min. in the GC/MS analysis.

[000116] FIG's. 91A and 91B illustrate illustrates the GC/MS selective ion chromatogram (m/z 508) and mass spectrum of pyrolysis product of Feedstock B atmospheric distillation fraction #7 (Table 3) concentrating undecamantanes.

[000117] FIG's. 92A, 92B and 92C illustrate a GC/MS selected ion chromatogram (m/z 508) and mass spectrum of an undecamantane component (mol. wt. 508) eluting at 21.07 min. and the mass spectrum of a methylundecamantane component (mol. wt. 522) eluting at 21.30 min.

[000118] FIG. 93 is a chart illustrating distillation cuts of a higher diamondoid-containing feedstock (Feedstock B, atmospheric distillation residue) showing cut selections to favor the enrichment of specific groups of higher diamondoids.

[000119] FIG. 94 shows the screw-like structures (right and left-handed) of [12341] hexamantane.

DETAILED DESCRIPTION OF THE INVENTION

[000120] This Detailed Description is presented in the following subsections:

[000121] Definitions

[000122] The Higher Diamondoids

[000123] Feedstocks

[000124] Isolation Processes

[000125] Utility

[000126] Examples

Definitions

[000127] As used herein, the following terms have the following meanings.

[000128] The term "diamondoid" refers to substituted and unsubstituted caged compounds of the adamantane series including adamantane, diamantane, triamantane, tetramantane, pentamantane, hexamantane, heptamantane, octamantane, nonamantane, decamantane, undecamantane, and the like and also including all isomers and stereoisomers thereof. Substituted diamondoids preferably comprise from 1 to 10 and more preferably 1 to 4 alkyl substituents.

[000129] The term "lower diamondoid components" or "adamantane, diamantane and triamantane components" refers to any and/or all unsubstituted and substituted derivatives of adamantane, diamantane and triamantane.

[000130] The term "higher diamondoid components" refers to any and/or all substituted and unsubstituted diamondoids corresponding to tetramantanes and above including tetramantanes, pentamantanes, hexamantanes, heptamantanes, octamantanes, nonamantanes,

decamantanes, undecamantanes, and the like including all isomers and stereoisomers thereof. Preferably, the higher diamondoids include substituted and unsubstituted tetramantanes, pentamantanes, hexamantanes, heptamantanes, octamantanes, nonamantanes, decamantanes and undecamantanes. FIG. 2 is a Table which shows representative higher diamondoids together with their molecular weights. The terms "diamondoid family", "tetramantane family" and the like are used to define a group of like "diamondoid components", having the same number of diamond crystal lattice cage units.

[000131] The term "tetramantane components" refer to any and/or all substituted and unsubstituted diamondoids corresponding to tetramantane.

[000132] The term "pentamantane components" refer to any and/or all substituted and unsubstituted diamondoids corresponding to pentamantane.

[000133] The term "non-ionized diamondoid components" refers to higher diamondoid components which do not carry a charge such as a positive charge generated during mass spectral analysis wherein the phrase "higher diamondoid components" is as defined herein.

[000134] The term "non-ionized tetramantane components" refers to tetramantane components which do not carry a charge such as a positive charge generated during mass spectral analysis.

[000135] The term "non-ionized pentamantane components and diamondoid components higher than pentamantane" refers to pentamantane components and higher diamondoid components larger than pentamantane which do not carry a charge such as a positive charge generated during mass spectral analysis.

[000136] The terms "selected higher diamondoid components" and the like refers to one or more substituted or unsubstituted higher diamondoids that are desired to be isolated or "enriched" in a product.

[000137] The terms "nonselected higher diamondoid components" and the like refer to those higher diamondoids that are not "selected higher diamondoids".

[000138] The term "enriched" when used to describe the state of purity of one or more higher diamondoid components refers to such materials at least partially separated from the feedstock, and in the case of "enriched" individual higher diamondoid components,

concentrated at least 25 and preferably at least 100 times the original concentration exhibited in the feedstock. Preferably "enriched" higher diamondoid or "enriched" higher diamondoid components make up at least 25%, especially at least 50% (i.e., 50-100%), more preferably at least 75% and yet more preferably at least 95% or even at least 99% by weight of the overall material in which they are present or in other words exhibit a weight purity of at least 25%, 50%, 75%, 95% or 99% of such material.

[000139] The term "feedstock" or "hydrocarbonaceous feedstock" refers to hydrocarbonaceous materials comprising recoverable amounts of higher diamondoids. Preferably, such feedstocks include oil, gas condensates, refinery streams, oils derived from reservoir rocks, oil shale, tar sands, and source rocks, and the like. Such components typically, but not necessarily, comprise one or more lower diamondoid components as well as non-diamondoid components. The latter is typically characterized as comprising components having a boiling point both below and above the lowest boiling point tetramantane which boils at about 350°C at atmospheric pressure. Typical feedstocks may also contain impurities such as sediment, metals including nickel, vanadium and other inorganics. They may also contain heteromolecules containing sulfur, nitrogen and the like. All of these nondiamondoid materials are included in "nondiamondoid components" as that term is defined herein.

[000140] The term "nonselected materials" refers to the collection of feedstock components that are not "selected higher diamondoids" and include "nondiamondoid components", "lower diamondoids" and "nonselected higher diamondoid" as these terms are defined herein.

[000141] The term "remove" or "removing" refers to processes for removal of non-diamondoid components and/or lower diamondoid components and/or nonselected higher diamondoid components from the feedstock. Such processes include, by way of example only, size separation techniques, distillation, evaporation either under normal or reduced pressure, well head separators, sorption, chromatography, chemical extraction, crystallization and the like. For example, Chen, et al.[4] disclose distillation processes for removing adamantane, substituted adamantane, diamantane, substituted diamantane, and triamantane from a hydrocarbonaceous feedstock. Size separation techniques include membrane separations, molecular sieves, gel permeation, size exclusion chromatography and the like.

[000142] The terms "distillation" or "distilling" refers to the fractionation processes in which materials are separated based on differences in vapor pressures, with high vapor pressure materials being taken overhead. Distillation can be carried out on hydrocarbonaceous feedstocks and on fractions otherwise obtained during the processing of hydrocarbonaceous feedstocks. In this context, most commonly, distillations are conducted under vacuum but also could be at atmospheric or even elevated pressures.

[000143] The terms "fractionation" and "fractionating" refer to processes in which materials in a mixture are separated from each other such as by differential solubility, differential vapor pressure, differential chromatographic affinity and the like.

[000144] The terms "pyrolysis" and "thermal treating to pyrolyze" and the like refer to either atmospheric, reduced pressure or elevated pressure heating of the feedstock or a feedstock fraction to thermally degrade a portion of one or more components in the feedstock.

[000145] The term "non-diamondoid components of a feedstock" refers to components of the feedstock or a feedstock fraction which are not diamondoid in character wherein the term "diamondoid" is as defined herein.

[000146] The term "retained" refers to retention of at least a portion of the higher diamondoid components found in the recovered feedstock when compared to the amount of such diamondoids found in the original feedstock. In a preferred embodiment, at least about 10 weight percent of the higher diamondoid components are retained in the recovered feedstock; more preferably, at least about 50 weight percent of the higher diamondoid components are retained in the recovered feedstock; and still more preferably, at least about 90 weight percent of the higher diamondoid components are retained in the recovered feedstock; each based on the total amount of such diamondoids found in the feedstock prior to treatment.

[000147] The term "chromatography" refers to any of a number of well known chromatographic techniques including, by way of example only, column or gravity chromatography (either normal or reverse phase), gas chromatography, high performance liquid chromatography, and the like.

[000148] The term "alkyl" refers to straight and branched chain saturated aliphatic groups typically having from 1 to 20 carbon atoms, more preferably 1 to 6 atoms ("lower alkyls"), as well as cyclic saturated aliphatic groups typically having from 3 to 20 carbon atoms and preferably from 3 to 6 carbon atoms ("lower alkyls" as well). The terms "alkyl" and "lower alkyl" are exemplified by groups such as methyl, ethyl, propyl, butyl, isopropyl, isobutyl, sec-butyl, t-butyl, n-heptyl, octyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl and the like.

The Higher Diamondoids

[000149] As shown in FIG. 1, higher diamondoids are bridged-ring cycloalkanes that have carbon-atom frameworks that can be superimposed on the diamond crystal lattice (FIG's. 1 and 4). They are the tetramers, pentamers, hexamers, heptamers, octamers, nonamers, decamers, etc. of adamantane (tricyclo[3.3.1.$1^{3,7}$]decane) or $C_{10}H_{16}$ in which various adamantane units are face-fused. The higher diamondoids can contain many alkyl substituents. These compounds have extremely rigid structures and have the highest stability of any compound with their formula. There are four tetramantane structures (FIG's. 2 and 3); *iso*-tetramantane [1(2)3], *anti*-tetramantane [121] and two enantiomers of *skew*-tetramantane [123] (FIG. 3) with the more general bracketed nomenclature for these diamondoids in accordance to a convention by Balaban *et al.*[15] There are ten pentamantanes (FIG. 5), nine have the molecular formula $C_{26}H_{32}$ (molecular weight 344), and among these nine there are three pairs of enantiomers represented by: [12(1)3], [1234], [1213] with the non-enantiomeric pentamantanes represented by: [12(3)4], [1(2,3)4], [1212]. There also exists a more strained pentamantane, [1231], represented by the molecular formula $C_{25}H_{30}$ (molecular weight 330). See FIG. 4. Hexamantanes exist with thirty-nine different structures (FIG. 6), twenty-eight having the molecular formula $C_{30}H_{36}$ (molecular weight 396) and of these, six are achiral; ten more strained hexamantanes have the molecular formula $C_{29}H_{34}$ (molecular weight 382) and the remaining hexamantane [12312] has the molecular formula $C_{26}H_{30}$ (molecular weight 342), also called cyclohexamantane because of its highly condensed circular structure. Heptamantanes are postulated to exist in one hundred and sixty possible structures; with eighty-five having the molecular formula $C_{34}H_{40}$ (molecular weight 448) (FIG. 7) and of these, seven are achiral, having no enantiomers. Only one of each of the two enantiomer structures of the chiral heptamantanes is shown in FIG. 7. Of the remaining heptamantanes, sixty-seven have the molecular formula $C_{33}H_{38}$

(molecular weight 434), and six have the molecular formula $C_{32}H_{36}$ (molecular weight 420). These two heptamantane families have structures showing greater internal bond strain, with correspondingly lower stabilities and are not shown in FIG. 7. The remaining two have the molecular formula $C_{30}H_{34}$ (molecular weight 394) (FIG. 7). Octamantanes possess eight of the "diamond crystal cage units" and exist within five families of different molecular weight core structures (FIG. 2). Among the octamantanes, eighteen have the molecular formula $C_{34}H_{38}$ (molecular weight 446). FIG. 8 shows each of the 446 molecular weight octamantane isomers. Other octamantanes have the molecular formula $C_{38}H_{44}$ (molecular weight 500). The remaining octamantane families, $C_{37}H_{42}$ (molecular weight 486), $C_{36}H_{40}$ (molecular weight 472) and $C_{33}H_{36}$ (molecular weight 432) show greater bond strain and correspondingly lower stability. Nonamantanes exist within six families of different molecular weights having the following molecular formulas: $C_{42}H_{48}$ (molecular weight 552), $C_{41}H_{46}$ (molecular weight 538), $C_{40}H_{44}$ (molecular weight 524), $C_{38}H_{42}$ (molecular weight 498), $C_{37}H_{40}$ (molecular weight 484) and $C_{34}H_{36}$ (molecular weight 444). Additionally, decamantane exists within families of seven different molecular weights. Among the decamantanes, there is a single decamantane having the molecular formula $C_{35}H_{36}$ (molecular weight 456) which is structurally compact in relation to the other decamantanes and has low internal bond strain. The other decamantane families have the molecular formulas: $C_{46}H_{52}$ (molecular weight 604), $C_{45}H_{50}$ (molecular weight 590), $C_{44}H_{48}$ (molecular weight 576), $C_{42}H_{46}$ (molecular weight 550), $C_{41}H_{44}$ (molecular weight 536) and $C_{38}H_{40}$ (molecular weight 496). Undecamantanes (FIG. 11) exist as molecular formulas $C_{50}H_{56}$ (molecular weight 656), $C_{49}H_{54}$ (molecular weight 642), $C_{48}H_{52}$ (molecular weight 628), $C_{46}H_{50}$ (molecular weight 602), $C_{45}H_{48}$ (molecular weight 588), $C_{42}H_{44}$ (molecular weight 548), $C_{41}H_{42}$ (molecular weight 534), $C_{39}H_{40}$ (molecular weight 508). More preferred and less preferred higher diamondoids (FIG. 2) are based on their internal bond strain and corresponding stabilities which is reflected by their relative concentrations in the various feedstocks.

Feedstocks

[000150] The higher diamondoids provided by this invention only exist in dilute concentrations in solution in petroleum feedstocks.

[000151] In the processes of this invention, a feedstock is selected such that said feedstock comprises recoverable amounts of one or more selected higher diamondoid components. Preferably, such feedstock comprises at least about 1 ppb of one or more higher diamondoid components, more preferably, at least about 25 ppb and still more preferably at least about 100 ppb. It is understood, of course, that feedstocks having higher concentrations of higher diamondoid components facilitate recovery of these components.

[000152] Preferred feedstocks include, for example, natural gas condensates and refinery streams having high concentrations of higher diamondoids. With regard to the latter, such refinery streams include hydrocarbonaceous streams recoverable from cracking processes, distillations, coking and the like. Particularly preferred feedstocks include gas condensates recovered from the Norphlet Formation in the Gulf of Mexico and from the LeDuc Formation in Canada.

[000153] In one embodiment, the feedstocks used in the processes of this invention typically comprise non-diamondoid components having boiling points both below and above the lowest boiling point higher diamondoid component selected for recovery as well as one or more lower diamondoid components. These feedstocks will usually contain a mixture of higher diamondoids. Depending upon which higher diamondoids are selected, some of these higher diamondoids may have boiling points below the selected higher diamondoid's boiling point. Typically, the lowest boiling point higher diamondoid component selected for recovery will have a boiling point of greater than about 335°C. In typical feedstocks, the concentration of lower diamondoids to higher diamondoids is generally about 250:1 or higher. Moreover as illustrated in FIG. 18, typical feedstocks comprising higher diamondoid components also comprise non-diamondoid components.

[000154] In such feedstocks, selected higher diamondoid components often cannot be effectively recovered directly from the feedstock because of their low concentrations relative to the nonselected components. Accordingly, the processes of this invention may entail removal of a sufficient amount of these contaminants from the feedstock under conditions to provide a treated feedstock from which the selected higher diamondoid components can be recovered.

Isolation Processes

[000155] The general isolation processes of higher diamondoids are shown in FIG. 12.

[000156] In one embodiment, the removal of contaminants includes distillation of the feedstock to remove non-diamondoid components as well as lower diamondoid components and in some cases other nonselected higher diamondoids having boiling points less than that of the lowest boiling point higher diamondoid component selected for recovery.

[000157] In a particularly preferred embodiment, the feedstock is distilled to provide cuts above and below about 335°C, atmospheric equivalent boiling point and, more preferably, above and below about 345 °C atmospheric equivalent boiling point. In either instance, the lower cuts, which are enriched in lower diamondoids and low boiling point non-diamondoid components are taken overhead and discarded and the higher boiling cut, which is enriched in higher diamondoids, is retained. It is understood, of course, that the temperature for the cut point during distillation is a function of pressure and that the above temperatures are referenced to atmospheric pressure. A reduced pressure will result in a lower distillation temperature to achieve the same cut point whereas an elevated pressure will result in a higher distillation temperature to achieve the same cut point. The correlation of pressure/temperature from atmospheric distillation to either reduced pressure or elevated pressure distillation is well within the skill of the art.

[000158] Distillation can be operated to fractionate the feedstocks and provide several cuts in a temperature range of interest to provide the initial enrichment of the selected higher diamondoids or groups of selected higher diamondoids. The cuts, which are enriched in one or more selected diamondoids or a particular diamondoid component of interest, are retained and may require further purification. The following Table illustrates representative fractionation points that may be used to enrich various higher diamondoids in overheads. In practice it may be advantageous to make wider temperature range cuts which would often contain groups of higher diamondoids which could be separated together in subsequent separation steps.

Fractionation Points

	Most Preferred		Preferred	
Higher Diamondoid	Lower Cut Temperature (°C)	Higher Cut Temperature (°C)	Lower Cut Temperature (°C)	Higher Cut Temperature (°C)
Tetramantanes	349	382	330	400
Pentamantanes	385	427	360	450
Cyclohexamantanes	393	466	365	500
Hexamantanes	393	466	365	500
Heptamantanes	432	504	395	540
Octamantanes	454	527	420	560
Nonamantanes	463	549	425	590
Decamantanes	472	571	435	610
Undecamantanes	499	588	455	625

	Useful	
Higher Diamondoid	Lower Cut Temperature (°C)	Higher Cut Temperature (°C)
Tetramantanes	300	430
Pentamantanes	330	490
Cyclohexamantanes	330	550
Hexamantanes	330	550
Heptamantanes	350	600
Octamantanes	375	610
Nonamantanes	380	650
Decamantanes	390	660
Undecamantanes	400	675

[000159] It shall be understood that substituted higher diamondoids may accordingly shift these preferred cut-point temperatures to higher temperatures due to the addition of substituent groups. Additional temperature refinements will allow for higher purity cuts for the diamondoid of interest. FIG. 93 provides further illustrations of how fractionation can provide cuts enriched in individual or multiple higher diamondoid components.

[000160] It will be further understood that fractionation can be stopped before a selected higher diamondoid is taken overhead. In this case the higher diamondoid can be isolated from the fractionation bottoms.

[000161] Other processes for the removal of lower diamondoids, unselected higher diamondoids, if any, and/or hydrocarbonaceous non-diamondoid components include, by way of example only, size separation techniques, evaporation either under normal or reduced pressure, crystallization, chromatography, well head separators, reduced pressure and the like. Removal processes can utilize the larger sizes of the higher diamondoids to effect separation of lower diamondoids therefrom. For example, size separation techniques using membranes will allow a feedstock retained in the membrane to selectively pass lower diamondoids across the membrane barrier provided that the pore size of the membrane barrier is selected to differentiate between compounds having the size of higher diamondoid components as compared to lower diamondoid components. The pore size of molecular sieves such as zeolites and the like can also be used to effect size separation.

[000162] In a preferred embodiment, the removal process provides for a treated feedstock having a ratio of lower diamondoid components to higher diamondoid components of no greater than 9:1; more preferably, no greater than 2:1; and even more preferably, the ratio is no greater than 1:1. Even more preferably, after removal of the lower diamondoid component(s) from the feedstock, at least about 10%, more preferably at least 50% and still more preferably at least 90% of the higher diamondoid components are retained in the feedstock as compared to that amount found in the feedstock prior to the removal.

[000163] When recovery of hexamantane and higher diamondoid components is desired and when the feedstock contains non-diamondoid contaminants, the feedstock will also be generally subjected to pyrolysis to effect removal of at least a portion of the hydrocarbonaceous non-diamondoid components from the feedstock. The pyrolysis effectively concentrates the amount of higher diamondoids in the pyrolytically treated feedstock thereby rendering their recovery possible (FIG. 18).

[000164] Pyrolysis is effected by heating the feedstock under vacuum conditions or in an inert atmosphere, at a temperature of at least about 390°C and, preferably, from about 400 to about 550°C, more preferably from about 400 to about 450°C , and especially 410 to 430°C; for a period of time to effect pyrolysis of at least a portion of the non-diamondoid components of the feedstock. The specific conditions employed are selected such that recoverable amounts of selected higher diamondoid components are retained in the feedstock. The selection of such conditions is well within the skill of the art.

[000165] Preferably, pyrolysis is continued for a sufficient period and at a sufficiently high temperature to thermally degrade at least about 10% of the non-diamondoid components (more preferably at least about 50% and even more preferably at least about 90%) from the pyrolytically treated feedstock based on the total weight of the non-diamondoid components in the feedstock prior to pyrolysis.

[000166] In yet another preferred embodiment, after pyrolysis of the feedstock, at least about 10%, more preferably at least about 50%, and still more preferably at least about 90% of the higher diamondoid components are retained in the feedstock after pyrolytic treatment compared to that amount found in the feedstock prior to pyrolytic treatment.

[000167] In a preferred embodiment, removal of lower diamondoids and low boiling point hydrocarbonaceous non-diamondoid components from the feedstock precedes pyrolytic treatment. However, it is understood, that the order of these procedures can be inverted such that pyrolysis occurs prior to removal of lower diamondoids from the feedstock.

[000168] The pyrolysis procedure, while a preferred embodiment, is not always necessary. This arises because the concentration of higher diamondoids can be sufficiently high in certain feedstocks that the treated feedstock (after removal of the lower diamondoid components) can be used directly in purification techniques such as chromatography, crystallization, etc. to provide higher diamondoid components. However, when the concentration or purity of higher diamondoid components in the feedstock is not at the level to effect such a recovery, then a pyrolytic step should be employed.

[000169] Even when pyrolysis is employed, it is preferred to further purify the recovered feedstock using one or more purification techniques such as chromatography, crystallization, thermal diffusion techniques, zone refining, progressive recrystalization, size separation and the like. In a particularly preferred process, the recovered feedstock is first subjected to gravity column chromatography using silver nitrate impregnated silica gel followed by HPLC using two different columns of differing selectivities to isolate the selected diamondoids and crystallization to provide crystals of the highly concentrated target higher diamondoids. Where higher diamondoid concentrations are not high enough for crystallization to occur, further concentration by, for example, preparative capillary gas chromatography may be necessary.

[000170] Enantioselective (chiral) stationary phases have been applied in chromatographic methods to effectuate further separations. High performance liquid chromatography methods also offer the possibility of using chiral solvents or additives to achieve resolution of enantiomers.

[000171] For example, separation of enantioneric forms of the high diamondoids can be achieved using several approaches. One such approach is spontaneous crystallization with resolution and mechanical separation. This approach to enantiomer resolution can be enhanced by preparation of derivatives or by the use of additives, chiral solvents, or various types of seed crystals. Another resolution option is chemical separation under kinetic or thermodynamic control. Other suitable processes for enantiomer resolution include chiral separations, which can be performed using a gas chromatographic (GC) see "Chiral Chromatography", T.E. Beesley, et. al, Wiley, Johnson & Sons, January 1998, incorporated herein by references, by high performance liquid chromatographic (HPLC) and by supercritical fluid chromatographic (SFC) techniques, see Supercritical fluids in Chromatography and Extraction", R.M. Smith, Elsevier Science, December 1997, incorporated herein by references.

Utility

[000172] The processes of this invention provide compositions enhanced in higher diamondoids. These higher diamondoids are useful in micro- and molecular-electronics and nanotechnology applications. In particular, the rigidity, strength, stability, thermal conductivity, variety of structural forms and multiple attachment sites shown by these molecules makes possible accurate construction of robust, durable, precision devices with nanometer dimensions. FIG. 15 shows the size and shapes of selected higher diamondoids relative to molecular components (Buckminsterfullerene and carbon nanotubes) employed in the development of molecular electronic devices.

[000173] The higher diamondoids are three-dimensional nanometer-sized units showing different diamond lattice arrangements. This translates into a great variety of shapes and sizes of these extremely rigid nanostructures, for example, [121(3)4] hexamantane is "T" shaped, [12134] is "L" shaped, and [1(2)3(1)2] is flat with four lobes. [12(3,4)12] heptamantane has a cross-shaped structure while [121234] is "L" shaped. [12312] hexamantane has a disc-like structure. [121321] heptamantane is disc-shaped with one co-

planar lobe, while [1213(1)21] octamantane is disc-shaped with two, opposing, co-planar lobes. [1232(1)3] octamantane is wedge-shaped. [121(2)32(1)3] nonamatane has a triangular plate-like structure. [1231241(2)3] decamantane is a perfect octagon, while [121231212] decamantane is rectangular plate-like structure. [123(1,2)42143] undecamantane is an elongated pyramid. A variety of other shapes exist among the higher diamondoids which may serve in applications in nanotechnology and nano-structured materials which depend upon specific geometries. The carbon-framework structures of the tetramantanes to the undecamantanes are shown in FIG's 3 to 11.

[000174] Higher diamondoids also include a series of rod-like structures of varying lengths. The tetramantane with the sequence "121" is the first member of this rod-shaped structural series, [1212] pentamantane is next, followed by [12121] hexamantane, and so on. Each added diamond cage increases the length of the rod by about 0.3 nm, with [1212] pentamantane having a length of about 1.1 nm.

[000175] The [1(2)3] tetramantane begins a more compact series, a flat-topped, pyramid-like structure (FIG. 3). [1(2,3)4] pentamantane (FIG. 5) follows this trend, being a perfect tetrahedral pyramid.

[000176] Higher diamondoids also include screw-like structures of varying lengths. The first chiral diamondoid is the tetramantane with sequence 123. We have specified the two enantiomers of 123 tetramantane as A and B. Their structures can also be implied by the sequences 123 and 124 by a modification of the Balaban nomenclature. These two diamondoids have left (counter-clockwise), i.e., tetramantane A, and right (clockwise) (tetramantane B)-hand helix or screw-like structures, both representing a partial-turn of the helix. Unfortunately, the Balaban nomenclature does not provide a way of specifying the left and right helical forms, only demonstrating that there exists two forms. This sequence continues with the progression 1234 and 1243 (i.e., A and B) for pentamantane (FIG. 5), 12341 and 12431 (again, A and B), for hexamantane (FIG. 6), and so on. The hexamantane members complete one full turn of a right and a left-handed helix for these screw-shaped nanostuctures (FIG 94).

[000177] These special structural characteristics set higher diamondoids apart from acyclic molecules, from condensed-ring systems and even from bridged-ring counterparts. The great stability, nanometer size, variable yet rigid geometry, well defined distances for places of

attachment, nonplanar bridgeheads lead to their unique features. Due to the rigidity, specialized geometry, 3-dimensional shape and nanometer size of the higher diamondoid components, it is expected that molecular aggregates and building blocks comprising them will enable construction and synthesis of a unprecedented array of desirable materials that will find applications in molecular electronic computing devices, reduced-size machines such as molecular robots and self-replicating manufacturing systems. Alternatively, the higher diamondoids may be used as novel materials of construction with special chemicals, optical, electric and thermal conductivity properties for coatings, film layering and other applications taking advantage of the diamond-like properties, etc. Novel uses of higher diamondoid-containing materials in the field of microelectronics are disclosed. Embodiments include, but not limited to, thermally conductive films in integrated circuit packaging, low-k dielectric layers in integrated circuit multilevel interconnents, thermally conductive adhesive films, thermally conductive films in thermoelectric cooling devises, passivation films for integrated circuit devices (ICs), and field emission cathodes.

[000178] In addition, these higher diamondoids can also be used in a high quality lubricating fluid which exhibits a high Viscosity Index and a very low pour point.[13] When so employed, these fluids comprise a fluid of lubricating viscosity and from about 0.1 to 10 weight percent diamondoids.

[000179] Still further, these higher diamondoids can be used as high density fuels in the manner described by Chung, et al.[14], incorporated herein by reference.

[000180] The following examples are offered to illustrate this invention and are not to be construed in any way as limiting the scope of this invention. Unless otherwise stated, all temperatures are in degrees Celsius.

EXAMPLES

[000181] As used herein and in the Figures, the following abbreviations have the following meanings. Any abbreviation not defined below has its generally accepted meaning.

API =	American Petroleum Institute	
atm eqv	=	atmospheric equivalent
btms	=	bottoms
EOR Traps	=	end of run traps
fid =	flame ionization detector	
g =	grams	
GC =	gas chromatography	
GC/MS	=	gas chromatography/mass spectroscopy
h =	hour	
HPLC	=	high performance liquid chromatography
HYD RDG	=	hydrometer reading
L =	liter	
min =	minute	
mL =	milliliters	
mmol	=	millimols
N =	normal	
pA =	pico amps	
ppb =	parts per billion	
ppm=	parts per million	
RI =	refractive index	
SIM DIS	=	simulated distillation
ST =	start	
TIC =	total ion current	
TLC	=	thin layer chromatography
VLT	=	vapor line temperature
VOL PCT	=	volume percent
v/v =	volume to volume	
wt =	weight	
WT PCT	=	weight percent

Introduction

[000182] The steps used in the various Examples are shown schematically in FIG. 12.

[000183] Example 1 describes a most universal route for isolating higher diamondoids components which can be applied to all feedstocks. This process uses HPLC (Step 7, FIG. 12) as its final isolation step.

[000184] Example 2 describes a variation of the process of Example 1 in which preparative gas chromatography (Step 7', FIG. 12) replaces HPLC as the final isolation step.

[000185] Example 3 describes a variation of the process of Example 1 in which the pyrolysis (Step 5, FIG. 12) is omitted. As shown optionally in FIG. 12, the liquid chromatographic step (Step 6, FIG. 12) is also omitted. These variations generally have applicability only with selected feedstocks and generally when tetramantanes, pentamantane and cyclohexamantane are the target higher diamondoids.

[000186] Example 4 describes yet another process variation in which the final products of Examples 1 and 3 are subjected to preparative gas chromatography purification to give further separation of higher diamondoid components (Step 8, FIG. 12).

[000187] Example 5 describes the enrichment and isolation of the tetramantane components.

[000188] Example 6 describes the enrichment and isolation of the pentamantane components.

[000189] Example 7 describes the enrichment and isolation of the hexamantane components.

[000190] Example 8 describes the enrichment and isolation of the heptamantane components.

[000191] Example 9 describes the enrichment and isolation of the octamantane components.

[000192] Example 10 describes the enrichment and isolation of the nonamantane components.

[000193] Example 11 describes the enrichment and isolation of the decamantane components.

[000194] Example 12 describes the enrichment and isolation of the undecamantane components.

[000195] It will be understood that it is possible to vary the order of the various distillation, chromatography and pyrolysis steps, although the order set forth in Example 1 has given the best results.

EXAMPLE 1

[000196] This Example has seven steps (see Flow Chart in FIG. 12).

[000197] Step 1. Feedstock selection

[000198] Step 2. GCMC assay development

[000199] Step 3. Feedstock atmospheric distillation

Step 4. Vacuum fractionation of atmospheric distillation residue

Step 5. Pyrolysis of isolated fractions

Step 6. Removal of aromatic and polar nondiamondoid components

[000203] Step 7. Multi-column HPLC isolation of higher diamondoids

a) First column of first selectivity to provide fractions enriched in specific higher diamondoids.

b) Second column of different selectivity to provide isolated higher diamondoids.

[000204] This example is written in terms of isolating several hexamantanes. As will be shown in Examples 5-12 it can be easily adapted to isolate the other higher diamondoids.

Step 1 – Feedstock Selection

[000205] Suitable starting materials were obtained. These materials included a gas condensate, Feedstock A (FIG. 16), and a gas condensate containing petroleum components, Feedstock B. Although other condensates, petroleums, or refinery cuts and products could have been used, these two materials were chosen due to their high diamondoid concentration, approximately 0.3 weight percent higher diamondoids, as determined by GC and GC/MS. Both feedstocks were light colored and had API gravities between 19 and 20° API.

Step 2 – GC/MS Assay Development

[000206] Feedstock A was analyzed using gas chromatography/mass spectrometry to confirm the presence of target higher diamondoids and to provide gas chromatographic retention times for these target materials. This information is used to track individual target higher diamondoids through subsequent isolation procedures. FIG. 13A is a table that lists typical GC/MS assay information for the hexamantanes (GC retention times, mass spectral molecular ion (M+) and base peak). This table (FIG. 13A) also contains similar GC/MS assay information for other higher diamondoids. While relative GC retention times are approximately constant, non-referenced GC retentions vary with time. It is recommended that GC/MS assay values be routinely updated especially when GC retention time drift is detected.

Step 3 – Feedstock Atmospheric Distillation

[000207] A sample of Feedstock B was distilled into a number of fractions based on boiling points to separate the lower boiling point components (nondiamondoids and lower diamondoids) and for further concentration and enrichment of particular higher diamondoids in various fractions. The yields of atmospheric distillate fractions of two separate samples of Feedstock B are shown in Table 1, below and are contrasted to simulated distillation yields. As seen from Table 1, the simulated distillation data is in agreement with the actual distillation data. The simulated distillation data were used to plan subsequent distillation processes.

TABLE 1: Yields of Atmospheric Distillation Fractions from Two Separate Runs of Feedstock B

Cut (°F)	Sim Dis Est.'d Yields (Wt %)	Feedstock B (Run 2) Yields (Wt %)	Difference
To 349	8.0	7.6	0.4
349 to 491	57.0	57.7	-0.7
491 to 643	31.0	30.6	0.4
643 and higher	4.0	4.1	-0.1

Cut (°F)	Sim Dis Est.'d Yields (Wt %)	Feedstock B (Run 1) Yields (Wt %)	Difference
To 477	63.2	59.3	3.9
477 to 515	4.8	7.3	-2.5
515 to 649	28.5	31.2	-2.7
649 and higher	3.5	2.1	1.4

Step 4 – Fractionation of Atmospheric Distillation Residue by Vacuum Distillation

[000208] The resulting Feedstock B atmospheric residium from Step 3 (comprising 2-4 weight percent of the original feedstock) was distilled into fractions containing higher diamondoids as shown in FIG's. 17 and 93). The feed to this high temperature distillation process was the atmospheric 650 °F + bottoms. Complete Feedstock B distillation reports are given in Tables 2A and 2B. Tables 3A and 3B illustrate the distillation reports for Feedstock B 650°F + distillation bottoms.

TABLE 2A. Distillation Report for Feedstock B

Feedstock B
Column Used: Clean 9" x 1.4" Protruded Packed

				DISTILLATION RECORD				NORMALIZED		ACTUAL	
CUT	VAPOR TEMP ST – END			WEIGHT G	VOLUME ml @ 60°F	API 60/60	DENSITY @ 60°F	WT PCT	VOL PCT	WT PCT	VOL PCT
1	226	-	349	67.0	80	38.0	0.8348	7.61	8.54	7.39	8.26
2	349	-	491	507.7	554	22.8	0.9170	57.65	59.12	55.98	57.23
3	491	-	643	269.6	268	9.1	1.0064	30.62	28.60	29.73	27.69
COL HOLDUP				0.2	0	6.6	1.0246	0.02	0.00	0.02	0.00
BTMS	643	+		36.1	35	6.6	1.0246	4.09	3.74	3.98	3.62
EOR TRAPS				0.0	0			0.00	0.00		0.00
TOTALS				880.6	937			100.00	100.00	97.09	96.80
LOSS				26.4	31					2.91	3.20
FEED				907.0	968	19.5	0.9371			100.00	100.00
BACK CALCULATED API AND DENSITY						19.1	0.9396				

TABLE 2B: Distillation Report for Feedstock B

Feedstock B
Column Used: Clean 9" x 1.4" Protruded Packed

TEMPERATURE DEGREES F			PRESSURE	REFLUX	CUT	VOLUME ml @ 60°F	WEIGHT G	API GRAVITIES		
VAPOR		POT	TORR	RATIO	NO			OBSERVED		60°F
VLT	ATM EQV							HYD RDG	TEMP °F	
93	225.8	262	50.000	3:1			START OVERHEAD			
198	349.1	277	50.000	3:1	1	80	67.0	39.6	80.0	38.0
321	490.8	376	50.000	3:1	2	554	507.7	24.1	80.0	22.8
Cut 2 looks Milky, White crystals form in Run Down Line. Heat Lamp applied to drip tube.										
Cool to transfer btms to smaller flask.										
208	437.7	323	10.000	3:1			START OVERHEAD			
378	643.3	550	10.000	3:1	3	268	269.6	9.9	75.0	9.1
Shutdown due to dry pot										
END OF RUN TRAPS						0	0.0			
VOLUME DISTILLED						902				
COLUMN HOLDUP						0	0.2	0.0	0.0	6.6
BOTTOMS						35	36.1	7.2	72.0	6.6
RECOVERED						937	880.6			
FEED CHARGED						968	907.0	20.7	80.0	19.5
LOSS						31	26.4			

TABLE 3A: Vacuum Distillation Report for Feedstock B

Feedstock B - Atmospheric distillation resid 650°F + bottoms
Column Used: Sarnia Hi Vac

TEMP ERATURE DEGREES F			PRESSURE	REFLUX	CUT	VOLUME ml	WEIGHT G	API GRAVITIES		
VAPOR		POT	TORR	RATIO	NO			OBSERVED		60° F
VLT	ATM EQV.					60° F		HYD RDG	TEMP °F	
315	601.4	350	5.000				START OVERHEAD			
344	636.8	382	5.000			300	READING			
342	644.9	389	4.000			500	READING			
344	656.3	395	3.300		1	639	666.4	7.8	138.0	4.1
353	680.1	411	2.500			400	READING			
364	701.6	430	2.100		2	646	666.9	9.4	138.0	5.6
333	736.0	419	0.400			200	READING			
336	751.9	432	0.300		3	330	334.3	12.4	139.0	8.3
391	799.9	468	0.500		4	173	167.7	19.0	139.0	14.5
411	851.6	500	0.270		5	181	167.3	26.8	139.0	21.7
460	899.8	538	0.360		6	181	167.1	27.0	139.0	21.9
484	950.3	569	0.222		7	257	238.4	26.2	139.0	21.2
Shut down distillation to check pot temperature limits with customer. (Drained trap material 5.3 grams)										
472	935.7	576	0.222				START OVERHEAD			
521	976.3	595	0.340		8	91	85.4	23.7	139.0	18.9
527	999.9	610	0.235		9	85	80.8	23.0	139.0	18.2
527	1025.6	624	0.130		10	98	93.8	21.6	139.0	16.9
Drained remaining trap material of 16.5 grams (~4 grams of water)										
		MID AND	END OF RUN TRAPS			20	17.8	(mathematically combined)		
			VOLUME DISTILLED			2701				
			COLUMN HOLDUP			4	4.0	0.0	0.0	3.4
			BOTTOMS			593	621.8	11.0	214.0	3.4
			RECOVERED			3298	3311.7			
			FEED CHARGED			3298	3326.3	18.0	234.0	8.6
			LOSS			-5	14.6			

TABLE 3B: Distillation Report for Feedstock B-btms

Feedstock B - Atmospheric distillation resid 650°F + bottoms
Column Used: Sarnia HiVac

CUT	VAPOR TEMP ST – END			WEIGHT G	VOLUME ml @ 60°F	API 60/60	DENSITY 60 °F	WT PCT	VOL PCT	WT PCT	VOL PCT
1	601	-	656	666.4	639	4.1	1.0435	20.12	19.38	20.03	19.40
2	656	-	702	666.9	646	5.6	1.0321	20.14	19.59	20.05	19.62
3	702	-	752	334.3	330	8.3	1.0122	10.09	10.01	10.05	10.02
4	752	-	800	167.7	173	14.5	0.9692	5.06	5.25	5.04	5.25
5	800	-	852	167.3	181	21.7	0.9236	5.05	5.49	5.03	5.50
6	852	-	900	167.1	181	21.9	0.9224	5.05	5.49	5.02	5.50
7	900	-	950	238.4	257	21.2	0.9267	7.25	7.79	7.17	7.80
8	950	-	976	85.4	91	18.9	0.9408	2.58	2.76	2.57	2.76
9	976	-	1000	80.8	85	18.2	0.9452	2.44	2.58	2.43	2.58
10	1000	-	1026	93.8	98	16.9	0.9535	2.83	2.97	2.82	2.98
COL HOLDUP				4.0	4	3.4	1.0489	0.12	0.12	0.12	0.12
BTMS	1026	+		621.8	593	3.4	1.0489	18.78	17.98	18.69	18.01
EOR TRAPS				17.8	20			0.54	0.61	0.54	0.61
TOTALS				3311.7	3298			100.00	100.00	99.56	100.15
LOSS				14.6	-5					0.44	-0.15
FEED				3326.3	3293	8.6	1.0100			100.00	100.00
BACK CALCULATED API & DENSITY						9.4	1.0039				

TABLE 4: Elemental Composition of Feedstock B

Analyses on Feedstock B 650+F Resid	
Measured	**Value**
Nitrogen	0.991 wt%
Sulfur	0.863 wt%
Nickel	8.61 ppm
Vanadium	< 0.2 ppm

[000209] Table 4 illustrates the partial elemental composition of Feedstock B atmospheric distillation (650°F) residue including some of the identified impurities. Table 4 displays the weight percent nitrogen, sulfur, nickel and vanadium in Feedstock B atmospheric distillation residue. Subsequent steps remove these materials.

Step 5 – Pyrolysis of Isolated Fractions

[000210] A high-temperature reactor was used to pyrolyze and degrade a portion of the nondiamondoid components in various distillation fractions obtained in Step 4 (FIG. 12) thereby enriching the diamondoids in the residue. The pyrolysis process was conducted at 450 °C for 19.5 hours. The gas chromatogram (FID) of fraction #6 (Table 3B) is shown in FIG. 18A. FIG. 18B is the chromatogram for the product of pyrolysis. A comparison of these chromatograms shows that pyrolysis has removed major nondiamondoid hydrocarbons and has significantly increased the higher diamondoid concentration, especially the hexamantanes. A 500 mL PARR® reactor from PARR Instrument Company, Moline, Illinois was used in this pyrolysis step.

Step 6 – Removal of Aromatic and Polar Nondiamondoid Components

[000211] The pyrolysate produced in Step 5 was passed through a silica-gel gravity chromatography column (using cyclohexane elution solvent) to remove polar compounds and asphaltenes (Step 6, FIG. 12). The use of a silver nitrate impregnated silica gel (10 weight percent $AgNO_3$) provides cleaner diamondoid-containing fractions by removing the free aromatic and polar components. While it is not necessary to use this chromatographic aromatic separation method, it facilitates subsequent steps.

Step 7 – Multi-column HPLC Isolation of Higher Diamondoids

[000212] An excellent method for isolating high-purity higher diamondoids uses two or more HPLC columns of different selectivities in succession.

[000213] The first HPLC system consisted of two Whatman M20 10/50 ODS columns operated in series using acetone as mobile phase at 5.00 mL/min. A series of HPLC fractions were taken (see FIG. 19). Fractions 36 and 37 were combined and taken for further purification on a second HPLC system. This combined fraction (36 and 37) contained hexamantanes #7, #11 and #13. (FIG. 19, also see FIG. 13B).

[000214] Further purification of this combined ODS HPLC fraction was achieved using a Hypercarb stationary phase HPLC column having a different selectivity in the separation of various hexamantanes than the ODS column discussed above. FIG. 20 shows elution times of the individual hexamantanes on the Hypercarb HPLC column (with acetone as a mobile phase).

[000215] The differences in elution times and elution order of hexamantanes on ODS and Hypercarb HPLC columns are seen by comparing these two FIG's. 19 and 20. For example, Hexamantanes #11 and #13 elute together on the ODS HPLC system (FIG. 19) but in separate fractions (fractions 32 and 27, respectively) on the Hypercarb system (FIG. 20).

[000216] The different elution orders and times of selected higher diamondoids on these two systems can be used to separate co-eluting higher diamondoids. It can also be used to remove impurities. Using this method on combined ODS HPLC fractions 36 & 37, appropriate Hypercarb HPLC fractions were taken thus providing high-purity hexamantane #13 (FIG's. 51A and 51B). Other ODS HPLC fractions and Hypercarb HPLC cut points could be used to isolate the remaining hexamantanes. This isolation strategy is also applicable to the other higher diamondoids although elution solvent compositions can vary.

[000217] The ODS and Hypercarb columns can also be used in reverse order for these isolations. By using similar methodology as above, i.e. fractionating hexamantane-containing ODS fractions using the Hypercarb or other suitable column and collecting at corresponding elution times can lead to the isolation of the remaining hexamantanes in high purity. This is also true of the other higher diamondoids from tetramantanes to undecamantanes, including substituted forms.

EXAMPLE 2

[000218] Steps 1, 2, 3, 4, 5 and 6 of Example 1 were repeated (FIG. 12). The following variation of Step 7 was then carried out.

Step 7':

[000219] A two-column preparative capillary gas chromatograph was used to isolate hexamantanes from the product of Example 1, Step 6. The cut times for the hexamantanes were set for the first preparative capillary the GC column, methyl silicone DB –1 equivalent, using the retention times and patterns from GC/MS assay (Example 1, Step 2). The results are shown in FIG. 42A, two cuts identified as "peaks cut and sent to column 2", were taken which contains two of the hexamantane components from Feedstock B. The preparative capillary gas chromatograph used was manufactured by Gerstel, Inc., Baltimore, Maryland, USA.

[000220] The first column was used to concentrate the higher diamondoids, such as hexamantanes by taking cuts that were then sent to the second column (see FIG. 42B illustrated for hexamantane #2 and #8). The second column, phenyl-methyl silicone, a DB-17 equivalent, further separated and purified the hexamantanes and then was used to isolate peaks of interest and retain them in individual traps (traps 1-6). GC trap fraction 1 contained crystals of hexamantane #2. GC trap fraction 3 contained crystals of hexamantane #8. Subsequent GC/MS analysis of trap #1 material (FIG. 43A and B) showed it to be high purity hexamantane #2 based upon the GC/MS assay of Step 2. Similarly, the GC analysis of trap #3 material (FIG. 44A and B) showed it to be primarily hexamantane #8. Photomicrographs of hexamantane #2 and #8 crystals (analyzed in FIG's. 43 and 44) are shown in FIG's. 45 and 46. This procedure could be repeated to isolate the other hexamantanes. This is also true of the other higher diamondoids.

EXAMPLE 3

[000221] Steps 1, 2, 3, and 4 (FIG. 12) of Example 1 were repeated using Feedstock A. Feedstock A is especially low in nondiamondoids in the atmospheric residue fraction recovered in Step 4. The pyrolysis Step (5) of Example 1 may be omitted especially when the higher diamondoids being sought are tetramantanes, pentamantanes and cyclohexamantane. In this case the fractions removed in Step 4 go directly to Steps 6 and 7

in Example 1 or directly to Step 7 in Example 2 (FIG. 12). This process variation can be applied to lower-boiling tetramantane-containing fractions of Feedstock B as well. However, pyrolysis is highly desirable where significant nondiamondoid components are present.

[000222] A fraction corresponding in cutpoint to fraction #1 of Step 4 (see distillation Table 3, Example 1 and FIG. 17) was taken from this feedstock. This fraction was further fractionated by preparative capillary gas chromatography similar to the processing shown in Step 7' of Example 2 (FIG. 12).

[000223] A two-column preparative capillary gas chromatograph was then used to isolate the target tetramantanes from the distillate fraction cleaned-up by column chromatography (Step 6, FIG. 12). Using the retention times and patterns from the GC/MS assay (from Step 2 of Example 1), the cut times for the target diamondoids (e.g., tetramantanes) were set for the first preparative capillary GC column, methyl silicone DB-1 equivalent. The results are shown on the top of FIG. 21 identified as cuts 1, 2 and 3.

[000224] The first column was used to concentrate the target diamondoids (e.g., tetramantanes) by taking cuts that were then sent to the second column (phenyl-methyl silicone, a DB-17 equivalent) (see the bottom of FIG. 21). The second column further separated and purified the target diamondoids and then sent them into individual traps (traps 1-6). GC traps 2, 4 and 6 contained the selected tetramantanes (FIG. 21).

[000225] The highly concentrated tetramantane higher diamondoids were then allowed to crystallize in the trap or dissolved and recrystallized from solution. Under the microscope at 30X magnification, crystals of the tetramantanes were visible in preparative GC traps 2, 4, and 6 (see FIG. 22). Where concentrations were not high enough for crystallization to occur, further concentration by preparative GC was necessary. The process would also work to isolate other higher diamondoids from Feedstock A.

EXAMPLE 4: Preparative GC of HPLC Fractions

[000226] With the heptamantanes, octamantanes and higher diamondoids, etc., it may be desirable to further fractionate the HPLC products obtained in Example 1, Step 7. This can be carried out using preparative capillary gas chromatography as described in Example 2, Step 7′.

[000227] The following higher diamondoid components were isolated and crystallized: all of the tetramantanes from both Feedstocks A and B, all pentamantanes (mol. wt. 344) isolated from Feedstock B; two hexamantane crystals (mol. wt. 396) isolated from Feedstock B; and, two heptamantane crystals (mol. wt. 394) isolated from Feedstock B, octamantane crystal (mol. wt 446) isolated from Feedstock B. As well as a nonamantane crystal (mol. wt. 498) and a decamantane crystal (mol. wt. 456) isolated from Feedstock B. The other higher diamondoid components could also be isolated using the procedures set forth in these examples.

EXAMPLE 5A: Isolation of Tetramantanes

[000228] The general processes of Examples 1 and 2 were used to enrich and isolate the tetramantanes.

[000229] In this example, pyrolysis Step 5 (FIG. 12) was not employed and the product of Step 4 went directly to column chromatography (Step 6 of Example 1). The column chromatography product was then treated as follows:

[000230] The eluent from the column chromatography of Step 6 was analyzed by GC/MS to determine the approximate GC retention times of tetramantane isomers. Individual tetramantanes were assigned a number according to their elution order in the GC/MS analysis. This reference number was used to identify individual tetramantanes in subsequent steps. Note that enantiomeric pairs are not resolved in this analysis and so these enantiomers (racemic mixtures) were assigned a single number for these purposes. GC retention times vary with changing columns and GC conditions and new reference retention time tables were prepared as needed using this procedure. Below is a table used in Example 5D procedures below.

Tetramantane Reference #	1	2	3
GCMS Retention Times (Min.)	11.28	11.84	12.36

[000231] A two-column preparative capillary gas chromatograph was then used to isolate tetramantanes from the distillate fractions cleaned-up by column chromatography. The results are shown in FIG. 21, identified as cuts 1, 2 and 3.

[000232] The first column was used to concentrate the tetramantanes by taking cuts that were then sent to the second column (see FIG. 21). The second column, phenyl-methyl silicone a DB-17 equivalent, further separated and purified the tetramantanes and then sent them into individual vials (traps 1-6). GC trap fractions 2, 4 and 6 were collected and further processed.

[000233] The highly concentrated tetramantanes were then allowed to crystallize from solution. Under the microscope at 30X magnification, crystals were visible in preparative GC trap fractions 2, 4, and 6 (see FIG. 22). Where concentrations were not high enough for crystallization to occur, further concentration by preparative GC was necessary. FIG.'s 22A, B and C illustrate photomicrographs of tetramantane crystals isolated from Feedstock A in trap, #2, #4 and #6 corresponding to tetramantane #1, #2, and #3 (respectively).

[000234] After obtaining crystals of suitable size, material could be sent for structural determination using X-ray diffraction. Enantiomeric tetramantanes can undergo further separations to resolve their two components as discussed previously.

EXAMPLE 5B: Enrichment of Tetramantanes Using Pyrolysis.

[000235] This example shows that pyrolysis (Step 5, Example 1, FIG. 12) can be useful in the isolation of tetramantanes.

[000236] Prior to pyrolysis, nondiamondoid components are present (FIG. 23A) in a tetramantane-containing fraction (distillation hold-up fraction similar in composition to Cut 1, FIG. 17). Pyrolysis degraded the nondiamondoid components to easily removable gas and coke-like solids. As shown in FIG. 23B, the nondiamondoid peaks are gone after pyrolysis.

[000237] Pyrolysis was conducted by heating the tetramantane-rich distillation cut under vacuum in the reactor at 450 °C for 20.4 hours.

EXAMPLE 5C: Isolation of Tetramantanes Using a Single HPLC System.

Isolations of diamondoids using HPLC

[000238] In addition to the gas chromatographic and pyrolysis methods described above, HPLC was also shown to provide sufficient enrichments of the tetramantanes to allow for their crystallization. Suitable columns for use are well known to those skilled in the art. In some cases, reverse-phase HPLC with acetone as mobile phase can be used to effect this purification. A preparative HPLC run of a Feedstock A, gas condensate, distillate fraction corresponding in cut point to Cut #1 (FIG. 17) was performed and the HPLC chromatogram recorded. Nine fractions where taken during the run. The HPLC columns used were two 25cm x 10mm I.D. Vydac octadecyl silane ODS columns operated in series (Vydac columns are manufactured by The Separations Group, Inc., CA, USA). A 20 microliter sample of a solution of the tetramantane-containing fraction at a concentration of 55 mg/mL was injected into the columns. The columns were set-up using acetone at 2.00 ml/min as a mobile phase carrier.

[000239] FIG. 24 (A,B) compares the gas chromatogram of the starting material (FIG. 24A) and HPLC fraction #6. HPLC Fraction #6 is significantly enriched in tetramantane FIG. 24B compared to the starting material (FIG. 24B compared to the starting material (FIG. 24A)). Tetramantane #2 in HPLC Fraction #6 is approaching a concentration sufficient to bring about its crystallization.

EXAMPLE 5D: Isolation of Individual Tetramantane Isomers by HPLC Using Multiple Columns with Different Selectivities

[000240] As shown in Example 5C, tetramantanes can be isolated using HPLC methods. In this example, HPLC columns of different selectivities were used to isolate single tetramantane isomers. FIG. 25 shows a preparative separation of the tetramantanes using an

octadecyl silane (ODS) HPLC column with acetone as a mobile phase. The distillation product used as starting material in Example 5B was the feedstock. Specifically, preparative HPLC fractionation of the holdup fraction from Feedstock B atmospheric distillation taken at about 650°F were performed. The first column consisted of two Whatman M20 10/50 (x2) ODS columns operated in series using acetone at 5.00 ml/min as mobile phase (@590 psi), 0.500 ml injection containing 56 mg/ml of the holdup fraction in acetone. The resulting chromatogram is shown on FIG. 25. Tetramantane #1 elutes first, tetramantane #3 elutes second and tetramantane #2 elutes last on the HPLC system (FIG. 25). The detector used was a differential refractometer. From this run, fraction 12 (FIG. 25) was taken for further purification.

[000241] Further purification of fraction 12 was achieved using Hypercarb-S HPLC columns which have a different specificity than the ODS column above, to isolate tetramantane #2 (FIG. 26). Two Hypercarb-S columns (manufactured by Thermo Hypersil, Penn, USA), 4.6mm I.D. x 250 mm, operated in series using acetone at 1.00 mL/min as mobile phase (@180 psi), 50 microliter injection of 4 mg/ml in acetone also using a differential refractometer. Tetramantane #3 elutes first, tetramantane #1 elutes second and tetramantane #2 elutes last on this Hypercarb HPLC system (FIG. 14). Tetramantane #2 was cut from this HPLC run (FIG. 26) and its purity illustrated in FIG.'s 28A and B. Hypercarb HPLC runs on ODS HPLC cut led to isolation of all the tetramantanes (enantiomers are separatable by chiral HPLC methods).

[000242] FIG. 27A shows the GC/MS total ion chromatogram (TIC) of an HPLC fraction containing tetramantane #1; and below it, FIG. 27B shows its mass spectrum. FIG. 29A shows the GC/MS total ion chromatogram (TIC) of an HPLC fraction containing isolated tetramantane #3; and below FIG. 29B shows the mass spectrum.

EXAMPLE 5E: Isolation of Substituted Tetramantanes

[000243] Alkyltetramantanes can be purified using methodologies described for nonalkylated tetramantanes given in Examples 5A to 5D. FIG. 30 shows an isolated monomethylated tetramantane with molecular weight of 306 yielding a mass spectrometric molecular ion of m/z 306, and shows a mass spectrometric loss of the methyl group giving the m/z 291 mass spectrometric fragment ion (indicative of a tetramantane moiety). This

alkylated compound was isolated by Hypercarb HPLC and shows a retention time of 11.46 minutes in our GC/MS system (FIG. 30). It may be necessary to use additional HPLC separations or preparative GC (as is Examples 3 and 4) to isolate some alkyltetramantanes.

EXAMPLE 6A: Isolation of Pentamantanes by Preparative Gas Chromatography

[000244] Steps 1-4 of Example 1 (FIG. 12) were repeated. In Step 5, 5.2 g. of Feedstock B 650°F + bottoms distillation cut 5 (Table 3, FIG. 18) was pyrolyzed under vacuum at 450°C for 16.7 hours. This product was then treated in accord with Example 1 Step 6.

[000245] The eluent from the column chromatography (Step 6) was analyzed by GC/MS to determine the GC retention times of pentamantane isomers. Individual pentamantane components with molecular weight 344 were assigned a number according to their elution order on this GC/MS analysis.

[000246] The two-column preparative capillary gas chromatograph was then used to isolate pentamantanes from the product of Step 6 above. An exemplary result is shown for pentamantane #1 in FIG. 31. The pentamantane #1-containing GC peak on the first column is identified as "peak cut and sent to column 2" in FIG. 31A.

[000247] The first column was used to concentrate the pentamantane by taking a cut that was then sent to the second column. The second column, phenyl-methyl silicone, a DB-17 equivalent, further separated the pentamantane #1 from other materials. The material in the peak of interest identified as "peak sent to trap" was sent to GC trap fraction 6 where crystals of pentamantane #1 accumulated (see FIG. 31B). GCMS analysis of trap #6 material (FIG. 32) showed it to be pentamantane #1 (in the pentamantane reference GCMS retention time system set-up for this preparative GC procedure, the first eluting pentamantane (#1) showed a retention time of 16.233 min. FIG's. 32A and B show the high purity of pentamantane #1 removed from GC trap 6. This procedure could be repeated to isolate the four other pentamantanes and three enantiomeric pairs which could be separated using chiral HPLC or other resolution techniques.

[000248] The highly concentrated pentamantanes crystallize either directly in the trap or from solution. Under the microscope at 30X magnification, crystals of pentamantane #1

were visible in preparative GC trap 6 (see FIG. 33A). These crystals were perfectly clear and showed high refractive index. Crystals of pentamantane #1 had never existed before this isolation. Where concentrations are not high enough for crystallization to occur, further concentration by preparative GC may be necessary. FIG. 33B is a photomicrograph of two pentamantanes that co-crystallized in a preparative GC trap.

[000249] After obtaining crystals of suitable size, non-enantiomeric pentamantane materials could be sent for structural determination using X-ray diffraction. Enantiomeric pentamantanes can undergo further separations to resolve their two components.

EXAMPLE 6B: Isolation of Pentamantanes by HPLC

[000250] Steps 1-6 of Example 6A were repeated. GC/MS assay reference numbers and retention times for the 344 molecular pentamantanes were as follows:

Pentamantane Reference #	1	2	3	4	5	6
GCMS Retention Times* (min.)	13.68	15.26	15.31	15.72	15.85	16.06

*(HP-5MS, 0.25 micron film, 0.25 mm I.D. x 30 m, helium carrier gas)

[000251] Pentamantane #1-containing ODS HPLC fractions indicated in FIG. 34 were further purified using Hypercarb HPLC (FIG. 35) to isolate pentamantane #1. FIG. 14 shows how ODS HPLC and Hypercarb HPLC can be used together to isolate the remaining pentamantanes. The ODS and Hypercarb columns can also be used in reverse order for this isolation. FIG. 36 shows the GC/MS total ion chromatogram (TIC) of the isolated pentamantane #1. The lower half of FIG. 36 illustrates the mass spectrum of the pentamantane #1 GC/MS peak. As indicated in FIG's. 14 and 34, the various remaining ODS HPLC fractions contain other pentamantanes. By using similar methodology as above, i.e. fractionating pentamantane containing ODS fractions using the Hypercarb (as indicated in FIG. 14) or another suitable column, and collecting at corresponding elution times, leads to the isolation of the remaining pentamantanes in high purity as shown in FIG's 37-41. Specifically, FIG. 37 illustrates GC/MS total ion chromatogram (TIC) and mass spectrum of pentamantane #2 isolated using two different HPLC columns; FIG. 38 illustrates GC/MS total ion chromatogram (TIC) and mass spectrum of pentamantane #3 isolated using two

different HPLC columns; FIG. 39 illustrates GC/MS total ion chromatogram (TIC) and mass spectrum of pentamantane #4 isolated using two different HPLC columns; FIG. 40 illustrates GC/MS total ion chromatogram (TIC) and mass spectrum of pentamantane #5 isolated using two different HPLC columns; and FIG. 41 illustrates GC/MS total ion chromatogram (TIC) and mass spectrum of pentamantane #6 isolated using two different HPLC columns. The enantiomeric pentamantanes are not resolved in GS/MS and therefore, these enantiomeric pairs are referenced within a single number. These enantiomers can be separated by chiral separation methods. In addition, as previously noted, there is a condensed isomer of pentamantane having a molecular weight of 330 which is more sterically strained and this appears in significantly lower concentrations. This pentamantane component has been observed in GC/MS analyses of distillation cut 5 pyrolysis product cleaned up using Step 6 of Example 1 (FIG. 12). This pentamantane component eluted at 14.4 minutes in the analysis of Example 1, Step 4 and could be isolated using procedures in this Example.

EXAMPLE 6C: Purification of Substituted Pentamantane

[000252] Substituted pentamantanes are present in Feedstocks A and B. Substituted pentamantanes can be enriched from these feedstocks and purified using methodologies described for nonalkylated pentamantanes in Examples 1-4. The monomethylated pentamantane enriched in this instance has a molecular weight of 358 (yielding a mass spectrometric molecular ion of m/z 358, and shows a mass spectrometric loss of the methyl group giving the m/z 343 mass spectrometric fragment ion indicative of a pentamantane moiety). This alkylated compound was enriched in ODS HPLC fraction #31 and could be further purified to form a crystal by an additional HPLC separation, or alternatively by a preparative GC procedure (as is Example 3).

EXAMPLE 7A: Isolation of Hexamantane Components

[000253] The purpose of this example is to demonstrate procedures which can be used for the enrichment and isolation of the thirty-nine hexamantane components. The process of Example 1 was repeated with the following changes. In Step 5, 34.4 g. of Feedstock B 650°F bottoms distillation cut #6 (Table 3, FIG. 18) was pyrolyzed under vacuum at 450°C for 17.3 hr.

[000254] The eluent from the column chromatography (Step 6) was analyzed by GC/MS to determine the GC retention times of hexamantanes. Individual hexamantane components with molecular weight 396 were assigned a number according to their elution order on this GC/MS assay. These hexamantanes were the most abundant and selected for convenience. Similar assays could be prepared for the other molecular weights. Hexamantane elution times ran between 17.88 min. (hexamantane #1) and 19.51 min. (hexamantane #7) in this GC/MS assay. Retention times vary with changing GC columns and conditions requiring remeasurement of retention times. FIG. 13A lists another GC/MS assay result for the hexamantane components,

[000255] A two-column preparative capillary gas chromatograph was used to isolate hexamantanes from the distillate fractions cleaned-up by column chromatography. The cut times for the hexamantanes were set for the first preparative capillary GC column, methyl silicone DB –1 equivalent, using the retention times and patterns from GC/MS assay. The results are shown in FIG. 42A, identified as "peak cut and sent to column 2" which contains two of the hexamantane fractions.

[000256] The first column was used to concentrate the hexamantanes by taking cuts that were then sent to the second column (see FIG. 42 illustrated for hexamantane #2 and #8). The second column, phenyl-methyl silicone a DB-17 equivalent, further separated and purified the hexamantanes and then was used to isolate peaks of interest and retain them into individual traps (traps 1-6). GC trap fraction 1 was collected and further processed for the separation of hexamantane #2. GC trap fraction 3 was collected and further processed for the separation of hexamantane #8. Subsequent GC/MS analysis of trap #1 material (FIG. 43) showed it to be hexamantane #2 based upon the earlier run GC/MS assay. Similarly, the GC analysis of trap #3 material (FIG. 44) showed it to be primarily hexamantane #8. This procedure could be repeated to isolate the other hexamantanes.

[000257] The highly concentrated hexamantanes were then allowed to crystallize either directly in the trap or from solution. Under the microscope at 30X magnification, crystals were visible in preparative GC trap fraction 1 (see FIG. 45). These crystals were perfectly clear and showed high refractive index. Crystals of hexamantane #2 had never existed before this isolation. Where concentrations are not high enough for crystallization to occur,

further concentration by preparative GC may be necessary. FIG. 46 is a photomicrograph of hexamantane #8 that crystallized in preparative GC trap 3. Crystals of hexamantane #8 had never existed before this isolation.

[000258] After obtaining crystals of suitable size, non-enantiomeric hexamantane components could be sent for structural determination using X-ray diffraction. Enantiomeric hexamantanes must undergo further separations to resolve the two components.

EXAMPLE 7B: Isolation of Hexamantanes Using a Single HPLC System.

[000259] The HPLC columns used were two 50cm x 20mm I.D. Whatman octadecyl silane (ODS) columns operated in series (Whatman columns are manufactured by Whatman Inc., USA). A 500 microliter sample of a solution of the cut 6 pyrolysis product saturated hydrocarbon fraction (54 mg), the product of Example 1, Step 6, was injected into the columns. The columns were setup using acetone at 5.00 ml/min as the mobile phase. Some of the HPLC fractions reached the purity necessary for individual hexamantanes to crystallize as shown for Hexamantane # 8 in ODS HPLC fraction # 39 (FIG. 47), Hexamantane # 10 in ODS HPLC fraction # 48 (FIG. 48) and Hexamantane # 6 in ODS HPLC fraction # 63 (FIG. 49). Alternatively a Hypercarb column (manufactured by Thermo Hypersil, Penn, USA) or other suitable column could be used to purify hexamantanes to concentrations necessary for them to crystallize. A preparative Hypercarb HPLC run of Feedstock B distillate cut 6 pyrolysis product saturated hydrocarbon fraction was performed and the HPLC chromatogram recorded using a differential refractometer. Fractions (e.g., FIG. 50) where taken during the run and showed that most hexamantanes display different elution times (verified by GC/MS analysis) from one another on the Hypercarb HPLC system (FIG. 20).

EXAMPLE 7C: Isolation of Hexamantanes Using Multiple HPLC Columns of Differing Selectivities

[000260] Hypercarb HPLC fractions were taken to obtain high purity hexamantane #13 demonstrated in FIG. 51. Other ODS HPLC fractions and Hypercarb HPLC cut points could be used to isolate the remaining hexamantanes. The ODS and Hypercarb columns can also be used in reverse order for this isolation. FIG. 52 shows the GC/MS total ion chromatogram (TIC) of the hexamantane #7 containing Hypercarb HPLC fraction. The lower half of FIG. 52 illustrates the mass spectrum of the GC/MS peak, demonstrating the high purity of the isolated hexamantane #7.

[000261] The various remaining ODS HPLC fractions (FIG. 19) containing other hexamantanes could be separated in the same way. By using similar methodology as above, i.e. fractionating hexamantane-containing ODS fractions using the Hypercarb or other suitable column and collecting at corresponding elution times can lead to the isolation of the remaining hexamantanes in high purity. This is also true of the hexamantanes with molecular weights of 382, "irregular" hexamantanes, that are in much lower abundance in our feedstocks than hexamantanes showing molecular weight of 396. FIG.'s 53 and 54 present reconstructed ion chromatograms for m/z 382 showing hexamantanes running at 18.30 min. and 18.07 min., respectively. FIG.'s 53 and 54 also show the corresponding mass spectra for these 18.30 min. and 18.07 min. peaks, demonstrating the presence of hexamantanes with a 382 molecular weight in the saturated hydrocarbon fraction from the product of pyrolytic processing of Feedstock B distillation fraction #6. The 382 molecular weight hexamantanes show internal bond strain, lower stability, and correspondingly lower concentrations than the 396 molecular weight hexamantanes, making the 382 molecular weight hexamantanes the less preferred hexamantanes.

[000262] The enantiomeric hexamantanes are not resolved in GS/MS and therefore, these enantiomeric pairs are referenced within a single number. These enantiomers can be isolated by chiral separation methods.

EXAMPLE 7D: Isolation of Substituted Hexamantanes

[000263] Substituted hexamantanes including alkylhexamantanes also are present in Feedstock A and B. These natural substituted hexamantanes have uses similar to the unsubstituted hexamantanes, can act as useful intermediates in various hexamantane applications (e.g., polymer production) and can be de-alkylated to yield the corresponding underivatized hexamantane. Accordingly, methods for the isolation of individual substituted hexamantane were devised and exemplified by the isolation of alkyl substituted components. Substituted hexamantanes, including alkylhexamantanes, can be isolated in high purity using a single HPLC separation of appropriate distillation cuts as exemplified by FIG. 55. FIG. 55 shows that fraction #55 from an ODS HPLC separation of the saturated hydrocarbon fraction from Feedstock B, distillation fraction 6 pyrolysis contains a methylated hexamantane in high purity. Monomethylated hexamantanes have a molecular weight of 410 (yielding a mass spectrometric molecular ion of m/z 410, and show a mass spectrometric loss of the methyl group giving the m/z 395 fragment ion (FIG. 55B)). Isolation of substituted hexamantane components by HPLC may require multiple columns with different selectivities. For example, the ODS and Hypercarb HPLC columns were run in succession to isolate the methylcyclohexamantane components (methyl-substituted mol. weight 342 hexamantane) from distillation cut 6-pyrolysis product saturated hydrocarbon fraction. From the first ODS HPLC run, fractions #23-26 were combined and taken for further purification on a second HPLC system. This combined fraction (FIG. 56) contained a mixture of hexamantane (mol. weight 342 referred to as cyclohexamantane), eluting on our GC/MS system at 12.31 minutes as well as three methylcyclohexamantanes (#1-3) eluting at 12.56, 12.72 and 13.03 minutes, respectively. Further purification of this mixture (i.e. combined ODS HPLC fractions #23-26) was achieved using a Hypercarb stationary phase HPLC column. A 50 microliter sample of approximately 1 mg of this combined fraction in acetone was injected into the Hypercarb column, 10 mm I.D. x 250 mm, operated using acetone at 3.00 mL/min as mobile phase (@480 psi) using a differential refractometer detector. In this Hypercarb system methylcyclohexamantane #1 elutes primarily in fractions 18-22 and methylcyclohexamantane #2 elutes primarily in fractions 23-25. Methylcyclohexamantane #1 and #2 where isolated in sufficient purity to form crystals. A GC/MS total ion chromatogram and mass spectrum of these compounds is illustrated in FIG.'s 57 and 59 and illustrated as crystals in photomicrographs in FIG's. 59 and 60. FIG. 59 illustrates a methylcyclohexamantane crystal precipitated from Hypercarb HPLC fractions #19-21 and

FIG. 60 illustrates a methylcyclohexamantane crystal precipitated from Hypercarb HPLC fractions #23.

[000264] Enantiomeric pairs must undergo further separations to resolve the two components. After obtaining crystals of suitable size, non-enantiomeric alkylhexamantanes can be sent for structural determination by x-ray crystallography.

EXAMPLE 8A: Isolation of Heptamantane Components

[000265] The eluent from the column chromatography (Step 6, FIG. 12) was analyzed by GC/MS to determine the GC retention times of heptamantanes. Individual heptamantane components with molecular weight 394 and 448 were assigned a number according to their elution order on our GC/MS assay (see FIG. 13A for representative assay values). Molecular weight 448 heptamantanes, the most abundant heptamantane family, were selected for convenience in this Example. Similar assays could be prepared for the other molecular weight heptamantanes.

[000266] A two-column preparative capillary gas chromatograph was then used to isolate heptamantanes from the distillate fractions cleaned-up by column chromatography. The cut times for the heptamantanes were set for the first preparative capillary GC column, methyl silicone DB –1 equivalent, using the retention times and patterns from GC/MS assay (from Step 2 above, FIG. 12). An exemplary result is shown in the top of FIG. 61, identified as "peak cut and sent to column 2" which contains two of the heptamantanes from Feedstock B.

[000267] The first column was used to concentrate the heptamantanes by taking cuts that were then sent to the second column (see FIG. 61 illustrated for heptamantanes #1 and #2). The second column, phenyl-methyl silicone a DB-17 equivalent, further separated and purified the heptamantane components and then was used to isolate peaks of interest and retain them in individual vials (traps 1-6). GC trap fraction 2 was collected and further processed for the separation of heptamantane #1. GC trap fraction 4 was collected and further processed for the separation of heptamantane #2. Subsequent GC/MS analysis of trap #2 material (FIG. 62) showed it to be heptamantane #1 based upon the earlier run GC/MS assay of step 4. Similarly, the GC analysis of trap #4 material (FIG. 63) showed it to be

heptamantane #2. This procedure could be repeated to isolate the other heptamantane components.

[000268] The highly concentrated heptamantanes were then allowed to crystallize either directly in the trap or from solution. Under the microscope at 30X magnification, crystals were visible in preparative GC trap fraction 2 (see FIG. 64). These crystals were perfectly clear and showed high refractive index. Crystals of heptamantane component #1 had never existed before this isolation. Where concentrations are not high enough for crystallization to occur, further concentration by preparative GC may be necessary. FIG. 65 is a photomicrograph of heptamantane component #2 that crystallized in preparative GC trap 4. Crystals of heptamantane component #2 had never existed before this isolation.

[000269] After obtaining crystals of suitable size, heptamantane materials could be sent for structural determination using X-ray diffraction. Enantiomeric heptamantanes can undergo further separations to resolve their two components.

EXAMPLE 8B: Purification of Single Heptamantane Isomers

[000270] HPLC was also shown to provide sufficient enrichments of some heptamantanes to allow for their crystallization.

[000271] The HPLC columns used were the same as those given in the other examples (ODS and Hypercarb). A 500 microliter sample of a solution of the cut 7 pyrolysis product saturated hydrocarbon fraction (product of Step 6, FIG. 12) was injected into the ODS columns. Pyrolysis of Cut 7 used 25.8 g. heated at 450°C for 16 hrs. Some of the ODS HPLC fractions reached the purity necessary for individual heptamantanes to crystallize as shown for heptamantane # 1 in ODS HPLC fraction # 45 (FIG. 66). Others, such as heptamantane # 2 in ODS HPLC fraction # 41 (FIG. 67), heptamantane # 9 in ODS HPLC fraction # 61 (FIG. 68), and heptamantane #10 in ODS HPLC fraction # 87 (FIG. 69), may require further separation on HPLC systems with different selectivities. Running the ODS fractions (FIG. 13B) on a Hypercarb column resulted in the purity necessary for individual heptamantane components to crystallize as shown for heptamantane component # 1 in Hypercarb HPLC fraction # 55 (FIG. 70) and heptamantane #2 (FIG. 71). The higher diamondoids in various HPLC fractions could be separated using further chromatographic

techniques including preparative gas chromatography and additional HPLC runs using columns of different selectivity as outlined below. Additionally other techniques known in the crystallization art could be utilized including but not limited to fractional sublimation, progressive recrystalization or zone refining could be used to purify the heptamantanes.

[000272] By using similar methodology as above, i.e. fractionating heptamantane-containing ODS fractions using the Hypercarb or other suitable columns and collecting at corresponding elution times can lead to the isolation of the remaining heptamantanes. This is also true of the heptamantanes with molecular weights of 420 and 434, that are in much lower abundance in our feedstocks than heptamantane components showing molecular weights of 394 and 448. A heptamantane component of molecular weight 420 shows up in ODS HPLC fraction #61 (FIG. 73A) with a very strong molecular ion in the mass spectrum (in this case m/z 420, FIG. 73B) for the m/z 420 component running at 16.71 min. The mass spectrum, with its prominent molecular ion and low number and abundance of fragments is characteristic of a diamondoid component.

EXAMPLE 8C: Isolation of Substituted Heptamantanes

[000273] Substituted heptamantanes including alkylheptamantanes also are present in Feedstock A and B. Alkylheptamantanes can be purified by removal of nondiamondoid impurities from feedstocks using pyrolysis as shown above. Certain alkylheptamantanes survive pyrolysis processing, as do the heptamantane components previously identified. Substituted heptamantanes including alkylheptamantanes can be isolated in high purity using a single HPLC separation as exemplified by FIG. 74. Monomethylated heptamantanes have a molecular weight of 408 (yielding a mass spectrometric molecular ion of m/z 408, and show a mass spectrometric loss of the methyl group giving the m/z 393 mass spectrometric fragment ion indicative of a heptamantane moiety (FIG. 74B).

EXAMPLE 9A: Isolation of Octamantane Components

[000274] An octamantane-enriched fraction from Step 6 was subjected to reverse-phase HPLC. In some cases, reverse-phase HPLC with acetone as mobile phase can be used to effect this purification. A preparative ODS HPLC run of Feedstock B distillate cut 7

pyrolysis product saturated hydrocarbon fraction (used in Example 8A) was performed and the HPLC chromatogram recorded using a differential refractometer. HPLC fractions were analyzed by GC/MS to determine octamantane HPLC elution times and monitor purity (see FIG. 13A for representative assay values). The HPLC columns used were the same ODS and Hypercarb systems used in previous examples. A 500 microliter sample of an acetone solution of the cut 7 pyrolysis product saturated hydrocarbon fraction (25 mg) was injected into the ODS columns. While using this HPLC system, some octamantanes reached purity needed for individual octamantanes to crystallize. For example, FIG. 75 illustrates a GC/MS total ion chromatogram and mass spectra of an HPLC fraction in which octamantane #1 has been purified to the point where it formed crystals (see FIG. 76). HPLC Fraction 63 yielded octamantane #3 and #5 together (FIG. 77), which co-crystallized from the fraction (FIG. 78).

[000275] For isolation in high purity of other octamantane components (for example FIG.'s 79 and 80), multiple columns can be employed, e.g. Hypercarb.

EXAMPLE 9B: Isolation of Substituted Octamantane Components

[000276] Alkyloctamantanes can be purified using methodologies described for non-alkylated octamantanes given in Examples 1 and 3. FIG. 81(A/B) shows that ODS HPLC fraction 94 contains a methylated octamantane in high purity. Monomethylated octamantanes have a molecular weight of 460 (yielding a mass spectrometric molecular ion of m/z 460, and show a mass spectrometric loss of the methyl group giving the m/z 445 mass spectrometric fragment ion indicative of an octamantane moiety (FIG. 81B). Also, where more than one alkyloctamantane is present in an ODS or Hypercarb HPLC fraction, an additional HPLC separation of that fraction or preparative GC procedure (as in Example 3) can yield high purity alkyloctamantanes.

EXAMPLE 10A: Isolation of Nonamantane Components

[000277] A preparative ODS HPLC run of Feedstock B distillate cut 7 pyrolysis product saturated hydrocarbon fraction was performed (material described in Example 8A) and the HPLC fractions were analyzed by GC/MS to determine nonamantane HPLC elution times (FIG. 82) and monitor purity. A 500 microliter sample of an acetone solution of the cut 7

pyrolysis product saturated hydrocarbon fraction (25 mg) was injected into the columns. The columns were set-up using acetone at 5.00 ml/min as a mobile phase carrier.

[000278] For isolation of nonamantane components in high purity, multiple HPLC columns can be employed. To illustrate this methodology, HPLC columns of different selectivities ODS and Hypercarb (as described in previous examples) were used in succession to isolate a single nonamantane. From the ODS HPLC run, the nonamantane containing fractions 84-88 (FIG. 13B) were combined for further purification on a Hypercarb HPLC system.

[000279] We injected a 50 microliter sample of approximately 1 mg of ODS HPLC combined fraction (84-88) in methylene chloride onto two Hypercarb columns, two 4.6 mm I.D. x 200 mm, operated in series using methylene chloride at 1.30 mL/min as mobile phase.

[000280] FIG. 83 shows the GC/MS total ion chromatogram (TIC) of the concentrated nonamantane containing Hypercarb HPLC fraction. The lower half of FIG. 83 illustrates the mass spectrum of the GC/MS peak. Nonamantane was isolated by a third HPLC run using the same Hypercarb stationary phase column but with a solvent consisting of methylene chloride/acetone (70:30 volume percent operating at 1.00 ml/min). The resulting isolated nonamantane crystal and corresponding mass spectrum are shown in FIG. 84.

[000281] By using a similar methodology as above, i.e. fractionating nonamantane containing ODS HPLC fractions using columns with different selectivities, such as the Hypercarb or other suitable columns, we isolated a molecular weight 498 nonamantane in high purity. This method could be repeated to isolate the nonamantanes with molecular weights of 552, and the nonamantanes of molecular weights 538, 484 and 444, which respectively are in lower abundance in our feedstocks. Note that enantiomeric nonamantanes are not resolved in GS/MS, however these enantiomers can be isolated by chiral separation methods.

EXAMPLE 10B: Isolation of Substituted Nonamantanes

[000282] Substituted nonamantanes also are present in Feedstock A and B. Alkylnonamantanes can be purified using methodologies described for non-alkylated nonamantanes. FIG. 85(A/B) shows methylated nonamantane in a pyrolysis product of distillate fraction #7. One type of monomethylated nonamantane has a molecular weight of 512 (yielding a mass spectrometric molecular ion of m/z 512, and show a mass spectrometric loss of the methyl group giving the m/z 497 mass spectrometric fragment ion indicative of a nonamantane moiety (FIG. 85B). More than one alkylnonamantane is present and these could be isolated using ODS or Hypercarb columns, an additional HPLC separation, or by preparative GC to yield high purity alkylnonamantanes.

EXAMPLE 11A: Isolation of Decamantane Components

[000283] A preparative ODS HPLC run of Feedstock B distillate cut 7 pyrolysis product saturated hydrocarbon fraction was performed and HPLC fractions were analyzed by GC/MS to determine decamantane HPLC elution times (FIG. 86) and monitor purity. The HPLC columns used were two 50cm x 20mm I.D. Whatman octadecyl silane (ODS) columns operated in series. A 500 microliter sample of an acetone solution of the cut 7 pyrolysis product saturated hydrocarbon fraction (25 mg) was injected into the columns. The columns were set-up using acetone at 5.00 ml/min as a mobile phase carrier.

[000284] For isolation of decamantane components in high purity, multiple HPLC columns can be employed. To illustrate this methodology, HPLC columns of different selectivities were used in succession to isolate a single decamantane. The first HPLC system consisted of the same ODS columns described previously. From this HPLC run, the decamantane containing fractions 74-83 were combined for further purification on a second HPLC system. Five such runs were completed and all decamantane containing fractions from the runs were combined. This combined fraction contained a molecular weight 456 decamantane and various impurities.

[000285] To purify the combined HPLC fractions 74-83 from the ODS HPLC separation, we injected a 50 microliter sample of approximately 1 mg of ODS HPLC combined fraction in acetone/methylene chloride (70:30 volume percent) onto two Hypercarb columns, 4.6 mm

I.D. x 200 mm, operated in series using acetone/methylene chloride (70:30 volume percent) at 1.00 mL/min as mobile phase (@480 psi).

[000286] FIG. 87 shows the GC/MS total ion chromatogram (TIC) of the concentrated decamantane-containing Hypercarb HPLC fraction eluting at 18.55 minutes. The lower half of FIG. 87 illustrates the mass spectrum of the GC/MS peak with a prominent peak at m/z 456. The resulting [1231241(2)3] molecular weight 456 decamantane crystal and mass spectrum are shown in FIG. 88. The 456 decamantane elutes before pentamantane #3 on the Hypercarb HPLC system due to its compact, low-surface area structure (FIG. 10). This property of 456 molecular weight decamantane makes possible its isolation in very high purity.

[000287] By using a similar methodology as above, i.e. fractionating decamantane-containing ODS HPLC fractions using columns with different selectivities, such as the Hypercarb or other suitable columns, we isolated a molecular weight 456 decamantane in high purity. This method could be repeated to isolate the decamantanes with molecular weights of 496 (shown in FIG. 89 in the saturated fraction of the pyrolysis product of distillate fraction #7) as well as molecular weights 550 or 604, and the decamantanes of molecular weights 536, 576 and 590, which respectively are in lower abundance in our feedstocks. Note that enantiomeric decamantanes are not resolved in GS/MS, however these enantiomers can be isolated by chiral separation methods.

EXAMPLE 11B: Isolation of Substituted Decamantanes

[000288] Substituted decamantanes also are present in Feedstock A and B. Alkyldecamantanes can be purified using methodologies described for non-alkylated decamantanes. FIG. 90 shows that saturated fraction of the pyrolysis product of distillate fraction #7 contains methylated decamantanes. One type of monomethylated decamantane has a molecular weight of 470 (yielding a mass spectrometric molecular ion of m/z 470). Also, where more than one alkyldecamantane is present in an ODS or Hypercarb HPLC fraction, an additional HPLC separation of that fraction or an alternative preparative GC procedure can yield high purity alkyldecamantanes.

EXAMPLE 12: Isolation of Undecamantane Components

[000289] For isolation of undecamantane components in high purity, multiple HPLC columns can be employed. This methodology was demonstrated using decamantane with HPLC columns of different selectivities used in succession to isolate a single decamantane (Example 11). An appropriate starting material, Feedstock B, distillation cut 7 pyrolysis product is shown to contain undecamantanes (FIG. 91).

[000290] The concentrated undecamantane from ODS HPLC fraction 100+ (FIG. 13B) is shown in FIG. 92. This fraction could be purified on a Hypercarb HPLC using a system (similar to that explained in Example 11) to isolate undecamantane. This method could be repeated to isolate the undecamantanes with molecular weights of 656 and/or 602, as well as molecular weights 642,628, 588, 548 or 534 which respectively are anticipated to be in lower abundance in our feedstocks.

WHAT IS CLAIMED IS:

1. An enriched selected higher diamondoid component neither including enriched unsubstituted anti-tetramantane, nor enriched cyclohexamantane.

2. The enriched selected higher diamondoid component of Claim 1, exhibiting a purity of at least 25% by weight.

3. A composition enriched in one or more selected higher diamondoid components, subject to the proviso that when there is only one selected higher diamondoid component it is neither unsubstituted anti-tetramantane nor unsubstituted cyclohexamantane.

4. The composition of Claim 3, wherein the one or more selected higher diamondoid components comprises at least 1% by weight of the composition.

5. The composition of Claim 3, wherein the one or more selected higher diamondoid components comprise at least 10% by weight of the composition.

6. The composition of Claim 3, containing from 50 to 100% by weight of one or more selected higher diamondoid components.

7. The composition of Claim 3, containing from 70 to 100% by weight of one or more selected higher diamondoid components.

8. The composition of Claim 3, containing from 95 to 100% by weight of one or more selected higher diamondoid components.

9. The composition of Claim 3, containing from 99 to 100% by weight of one or more selected higher diamondoid components.

10. The composition of Claims 3-9, wherein the one or more selected higher diamondoid components are a single selected higher diamondoid component.

11. A composition comprising diamondoids enriched in one or more selected higher diamondoid components relative to the total amount of diamondoid, subject to the proviso that when there is only one selected higher diamondoid component, it is neither unsubstituted anti-tetramantane nor cyclohexamantane.

12. The composition of Claim 11, wherein at least about 25% weight percent of the total amount of diamondoids is the one or more selected higher diamondoids.

13. The composition of Claim 12, wherein the one or more selected higher diamondoid components are a plurality of the components in a single diamondoid family.

14. The composition of Claim 12, wherein the one or more selected higher diamondoid components are a single selected higher diamondoid component.

15. The composition of Claims 1-14, wherein the selected higher diamondoid components comprise one or more tetramantane components.

16. The composition of Claim 15, wherein the one or more tetramantane components are a single tetramantane component.

17. The composition of Claim 16, wherein the single tetramantane component is *iso*-tetramantane.

18. The composition of Claim 16, wherein the single tetramantane component is *skew*-tetramantane.

19. The composition of Claim 16, wherein the single tetramantane component is a single enantiomer of *skew*-tetramantane.

20. The composition of Claim 15, wherein the tetramantane components comprise substituted tetramantane components.

21. Enriched *iso*-tetramantane.

22. Enriched *skew*-tetramantane enantiomer A.

23. Enriched skew-tetramantane enantiomer B.

24. The enriched tetramantane component of Claims 21-23, exhibiting a purity of at least 25%.

25. The enriched tetramantane component of Claims 21-23, in crystalline form.

26. The composition of Claims 1-14, wherein the selected higher diamondoid components comprise one or more pentamantane components.

27. The composition of Claim 26, wherein the one or more pentamantane components are a single pentamantane component.

28. The composition of Claim 26, wherein the one or more pentamantane components are isolated optical isomers.

29. The composition of Claim 26, wherein the one or more pentamantane components are isomeric pentamantane components.

30. The composition of Claim 26, wherein the one or more pentamantane components is the nonisomeric pentamantane component represented by the formula $C_{25}H_{30}$.

31. An enriched pentamantane component.

32. The enriched pentamantane component of Claim 31, exhibiting a purity of at least 25% by weight.

33. The enriched pentamantane component of Claim 31, in crystalline form.

34. The enriched pentamantane component of Claim 31, wherein the pentamantane component is [1231] pentamantane.

35. The enriched pentamantane component of Claim 31, wherein the pentamantane component is [1213] enantiomer A pentamantane.

36. The enriched pentamantane component of Claim 31, wherein the pentamantane component is [1213] enantiomer B pentamantane.

37. The enriched pentamantane component of Claim 31, wherein the pentamantane component is [1234] enantiomer A pentamantane.

38. The enriched pentamantane component of Claim 31, wherein the pentamantane component is [1234] enantiomer B pentamantane.

39. The enriched pentamantane component of Claim 31, wherein the pentamantane component is [12(1)3] enantiomer A pentamantane.

40. The enriched pentamantane component of Claim 31, wherein the pentamantane component is [12(1)3] enantiomer B pentamantane.

41. The enriched pentamantane component of Claim 31, wherein the pentamantane component is [1212] pentamantane.

42. The enriched pentamantane component of Claim 31, wherein the pentamantane component is [1(2,3)4] pentamantane.

43. The enriched pentamantane component of Claim 31, wherein the pentamantane component is [12(3)4] pentamantane.

44. The enriched pentamantane component of Claim 31, wherein the pentamantane component is an unsubstituted pentamantane component.

45. The enriched pentamantane component of Claim 31, wherein the pentamantane component is a substituted pentamantane component.

46. The composition of Claims 1-14, wherein the selected higher diamondoid components comprise one or more hexamantane components.

47. The composition of Claim 46, wherein the one or more hexamantane components are a single hexamantane component.

48. The composition of Claim 46, wherein the one or more hexamantane components are isolated optical isomers.

49. The composition of Claim 46, wherein the one or more hexamantane components are isomeric hexamantane components.

50. The composition of Claim 46, wherein the one or more hexamantane components are one or more of the hexamantane components represented by the formula $C_{30}H_{36}$.

51. The composition of Claim 46, wherein the one or more hexamantane components are one or more of the hexamantane components represented by the formula $C_{29}H_{34}$.

52. An enriched hexamantane component represented by the formulas $C_{30}H_{36}$ or $C_{29}H_{34}$ with and without substitution.

53. The enriched hexamantane component of Claim 52, exhibiting a purity of at least 25% by weight.

54. The enriched hexamantane component of Claim 52, in crystalline form.

55. The enriched hexamantane component of Claim 52, represented by the formula $C_{29}H_{36}$.

56. The enriched hexamantane component of Claim 52, represented by the formula $C_{30}H_{36}$.

57. The enriched hexamantane component of Claim 56, selected from the group consisting of

[1(2)314] enantiomer A hexamantane

[1(2)314] enantiomer B hexamantane

[12(1)32] enantiomer A hexamantane

[12(1)32] enantiomer B hexamantane

[12(1)34] enantiomer A hexamantane

[12(1)34] enantiomer B hexamantane

[12(1,3)4] hexamantane

[12(3)14] enantiomer A hexamantane

[12(3)14] enantiomer B hexamantane

[121(2)3] enantiomer A hexamantane

[121(2)3] enantiomer B hexamantane

[12123] enantiomer A hexamantane

[12123] enantiomer B hexamantane

[12131] enantiomer A hexamantane

[12131] enantiomer B hexamantane

[12134] enantiomer A hexamantane

[12134] enantiomer B hexamantane

[12324] enantiomer A hexamantane

[12324] enantiomer B hexamantane

[12341] enantiomer A hexamantane

[12341] enantiomer B hexamantane

[1(2)3(1)2] hexamantane

[12(3)12] hexamantane

[121(3)4] hexamantane

[12121] hexamantane

[12321] hexamantane

[1(2)3(1)4] enantioner A hexamantane

[1(2)3(1)4] enantiomer B hexamantane

58. The enriched hexamantane component of Claim 52, wherein the hexamantane component is an unsubstituted hexamantane component.

59. The enriched hexamantane component of Claim 52, wherein the hexamantane component is a substituted hexamantane component.

60. The enriched substituted cyclohexamantane component.

61. The composition of Claims 1-14, wherein the selected higher diamondoid components comprise one or more heptamantane components.

62. The composition of Claim 61, wherein the one or more heptamantane components are a single heptamantane component.

63. The composition of Claim 61, wherein the one or more heptamantane components are isolated optical isomers.

64. The composition of Claim 61, wherein the one or more heptamantane components are isomeric heptamantane components.

65. The composition of Claim 61, wherein the one or more heptamantane components are one or more isomeric heptamantane components represented by the formula $C_{30}H_{34}$.

66. The composition of Claim 61, wherein the one or more heptamantane components are one or more isomeric heptamantane components represented by the formula $C_{32}H_{36}$.

67. The composition of Claim 61, wherein the one or more heptamantane components are one or more isomeric heptamantane components represented by the formula $C_{33}H_{38}$.

68. The composition of Claims 61, wherein the one or more heptamantane components are one or more isomeric heptamantane components represented by the formula $C_{34}H_{40}$.

69. An enriched heptamantane component.

70. The enriched heptamantane component of Claim 69, exhibiting a purity of at least 25% by weight.

71. The enriched heptamantane component of Claim 69, in crystalline form.

72. The enriched heptamantane component of Claim 69, wherein the heptamantane component has a molecular weight of 394.

73. The enriched heptamantane component of Claim 69, wherein the heptamantane component is [121321] heptamantane.

74. The enriched heptamantane component of Claim 69, wherein the heptamantane component is [123124] heptamantane.

75. The enriched heptamantane component of Claim 69, wherein the heptamantane component is an unsubstituted component.

76. The enriched heptamantane component of Claim 69, wherein the heptamantane component is an substituted component.

77. The composition of Claims 1-14, wherein the selected higher diamondoid components comprise one or more octamantane components.

78. The composition of Claim 77, wherein the one or more octamantane components are a single octamantane component.

79. The composition of Claim 77, wherein the one or more octamantane components are isolated optical isomers.

80. The composition of Claim 77, wherein the one or more octamantane components are isomeric octamantane components.

81. The composition of Claim 77, wherein the one or more octamantane components are one or more isomeric octamantane components represented by the formula $C_{33}H_{36}$.

82. The composition of Claim 77, wherein the one or more octamantane components are one or more isomeric octamantane components represented by the formula $C_{34}H_{38}$.

83. The composition of Claim 77, wherein the one or more octamantane components are one or more isomeric octamantane components represented by the formula $C_{36}H_{40}$.

84. The composition of Claim 77, wherein the one or more octamantane components are one or more isomeric octamantane components represented by the formula $C_{37}H_{42}$.

85. The composition of Claim 77, wherein the one or more octamantane components are one or more isomeric octamantane components represented by the formula $C_{38}H_{44}$.

86. An enriched octamantane component.

87. The enriched octamantane component of Claim 86, exhibiting a purity of at least 25% by weight.

88. The enriched octamantane component of Claim 86, in crystalline form.

89. The enriched octamantane component of Claim 86, wherein the octamantane component is an unsubstituted octamantane component.

90. The enriched octamantane component of Claim 86, wherein the octamantane component is a substituted octamantane component.

91. The composition of Claims 1-14, wherein the selected higher diamondoid components comprise one or more nonamantane components.

92. The composition of Claim 91, wherein the one or more nonamantane components are a single nonamantane component.

93. The composition of Claim 91, wherein the one or more nonamantane components are isolated optical isomers.

94. The composition of Claim 91, wherein the one or more nonamantane components are isomeric nonamantane components.

95. The composition of Claim 91, wherein the one or more nonamantane component is the isomeric nonamantane component represented by the formula $C_{34}H_{36}$.

96. The composition of Claim 91, wherein the one or more nonamantane components are one or more isomeric nonamantane components represented by the formula $C_{37}H_{40}$.

97. The composition of Claim 91, wherein the one or more nonamantane components are one or more isomeric nonamantane components represented by the formula $C_{38}H_{42}$.

98. The composition of Claim 91, wherein the one or more nonamantane components are one or more isomeric nonamantane components represented by the formula $C_{40}H_{44}$.

99. The composition of Claim 91, wherein the one or more nonamantane components are one or more isomeric nonamantane components represented by the formula $C_{41}H_{46}$.

100. The composition of Claim 91, wherein the one or more nonamantane components are one or more isomeric nonamantane components represented by the formula $C_{42}H_{48}$.

101. An enriched nonamantane component.

102. The enriched nonamantane component of Claim 101, exhibiting a purity of at least 25% by weight.

103. The enriched nonamantane component of Claim 101, in crystalline form.

104. The enriched nonamantane component of Claim 101, wherein the nonamantane component is an unsubstituted nonamantane component.

105. The enriched nonamantane component of Claim 101, wherein the nonamantane component is a substituted nonamantane component.

106. The composition of Claims 1-14, wherein the selected higher diamondoid components comprise one or more decamantane components.

107. The composition of Claim 106, wherein the one or more decamantane components are a single decamantane component.

108. The composition of Claim 106, wherein the one or more decamantane components are isolated optical isomers.

109. The composition of Claim 106, wherein the one or more decamantane components are isomeric decamantane components.

110. The composition of Claim 106, wherein the one or more decamantane components is the nonisomeric decamantane component represented by the formula $C_{35}H_{36}$.

111. The composition of Claim 106, wherein the one or more decamantane components are one or more of the isomeric decamantane components represented by the formula $C_{38}H_{40}$.

112. The composition of Claim 106, wherein the one or more decamantane components are one or more of the isomeric decamantane components represented by the formula $C_{41}H_{44}$.

113. The composition of Claim 106, wherein the one or more decamantane components are one or more of the isomeric decamantane components represented by the formula $C_{42}H_{46}$.

114. The composition of Claim 106, wherein the one or more decamantane components are one or more of the isomeric decamantane components represented by the formula $C_{44}H_{48}$.

115. The composition of Claims 106, wherein the one or more decamantane components are one or more of the isomeric decamantane components represented by the formula $C_{45}H_{50}$.

116. The composition of Claim 106, wherein the one or more decamantane components are one or more of the isomeric decamantane components represented by the formula $C_{46}H_{52}$.

117. An enriched decamantane component.

118. The enriched decamantane component of Claim 117, exhibiting a purity of at least 25% by weight.

119. The enriched decamantane component of Claim 117, in crystalline form.

120. The enriched decamantane component of Claim 117, wherein the decamantane component is [1231241(2)3] decamantane.

121. The enriched decamantane component of Claim 117, wherein the decamantane component is an unsubstituted decamantane component.

122. The enriched decamantane component of Claim 117, wherein the decamantane component is a substituted decamantane component.

123. The composition of Claims 1-14, wherein the selected higher diamondoid components comprise one or more undecamantane components.

124. The composition of Claim 123, wherein the one or more undecamantane components are a single undecamantane component.

125. The composition of Claim 123, wherein the one or more undecamantane components are isolated optical isomers.

126. The composition of Claim 123, wherein the one or more undecamantane components are isomeric undecamantane components.

127. The composition of Claim 123, wherein the one or more undecamantane component are one or more isomeric undecamantane components represented by the formula $C_{39}H_{40}$.

128. The composition of Claim 123, wherein the one or more undecamantane components are one or more isomeric undecamantane components represented by the formula $C_{41}H_{42}$.

129. The composition of Claim 123, wherein the one or more undecamantane components are one or more nonisomeric undecamantane components represented by the formula $C_{42}H_{44}$.

130. The composition of Claim 123, wherein the one or more undecamantane components are one or more nonisomeric undecamantane components represented by the formula $C_{45}H_{48}$.

131. The composition of Claim 123, wherein the one or more undecamantane components are one or more nonisomeric undecamantane components represented by the formula $C_{46}H_{50}$.

132. The composition of Claim 123, wherein the one or more undecamantane components are one or more nonisomeric undecamantane components represented by the formula $C_{48}H_{52}$.

133. The composition of Claim 123, wherein the one or more undecamantane components are one or more nonisomeric undecamantane components represented by the formula $C_{49}H_{54}$.

134. The composition of Claim 123, wherein the one or more undecamantane components are one or more nonisomeric undecamantane components represented by the formula $C_{50}H_{56}$.

135. An enriched undecamantane component.

136. The enriched undecamantane component of Claim 135, exhibiting a purity of at least 25% by weight.

137. The enriched undecamantane component of Claim 135, in crystalline form.

138. The enriched undecamantane component of Claim 135, wherein the undecamantane component is an unsubstituted undecamantane component.

139. The enriched undecamantane component of Claim 135, wherein the undecamantane component is a substituted undecamantane component.

140. A process for recovering a composition enriched in higher diamondoid components, which process comprises:

a. selecting a feedstock comprising recoverable amounts of higher diamondoid components;

b. removing a sufficient amount of components from the feedstock having a boiling point less than the lowest boiling higher diamondoid component of interest under conditions to provide a treated feedstock from which higher diamondoid components can be recovered; and

c. recovering higher diamondoid components from said treated feedstock by separation techniques selected from the group consisting of chromatographic techniques, thermal diffusion techniques, zone refining, progressive recrystalization and size separation techniques.

141. A process for recovering an enriched higher diamondoid of Claim 1, which comprises:

a. selecting a feedstock comprising recoverable amounts of a higher diamondoid component or components selected for recovery, nondiamondoid components and components having a boiling point less than the lowest boiling point higher diamondoid component selected for recovery;

b. removing from the feedstock a sufficient amount of components having a boiling point less than the lowest boiling point higher diamondoid component selected for recovery under conditions wherein recoverable amounts of the higher diamondoid component or components selected for recovery are retained in the treated feedstock; and

c. thermally treating the feedstock recovered in b) above to pyrolyze at least a sufficient amount of nondiamondoid components therefrom to permit recovery of the selected higher diamondoid component or components from the pyrolytically treated feedstock wherein the pyrolysis is conducted under conditions to provide a treated feedstock retaining recoverable amounts of the selected higher diamondoid component or components.

d. recovering selected higher diamondoid components from said treated feedstock by separation techniques selected from the group consisting of chromatographic techniques, thermal diffusion techniques, zone refining, progressive recrystalization and size separation techniques.

FIG. 1

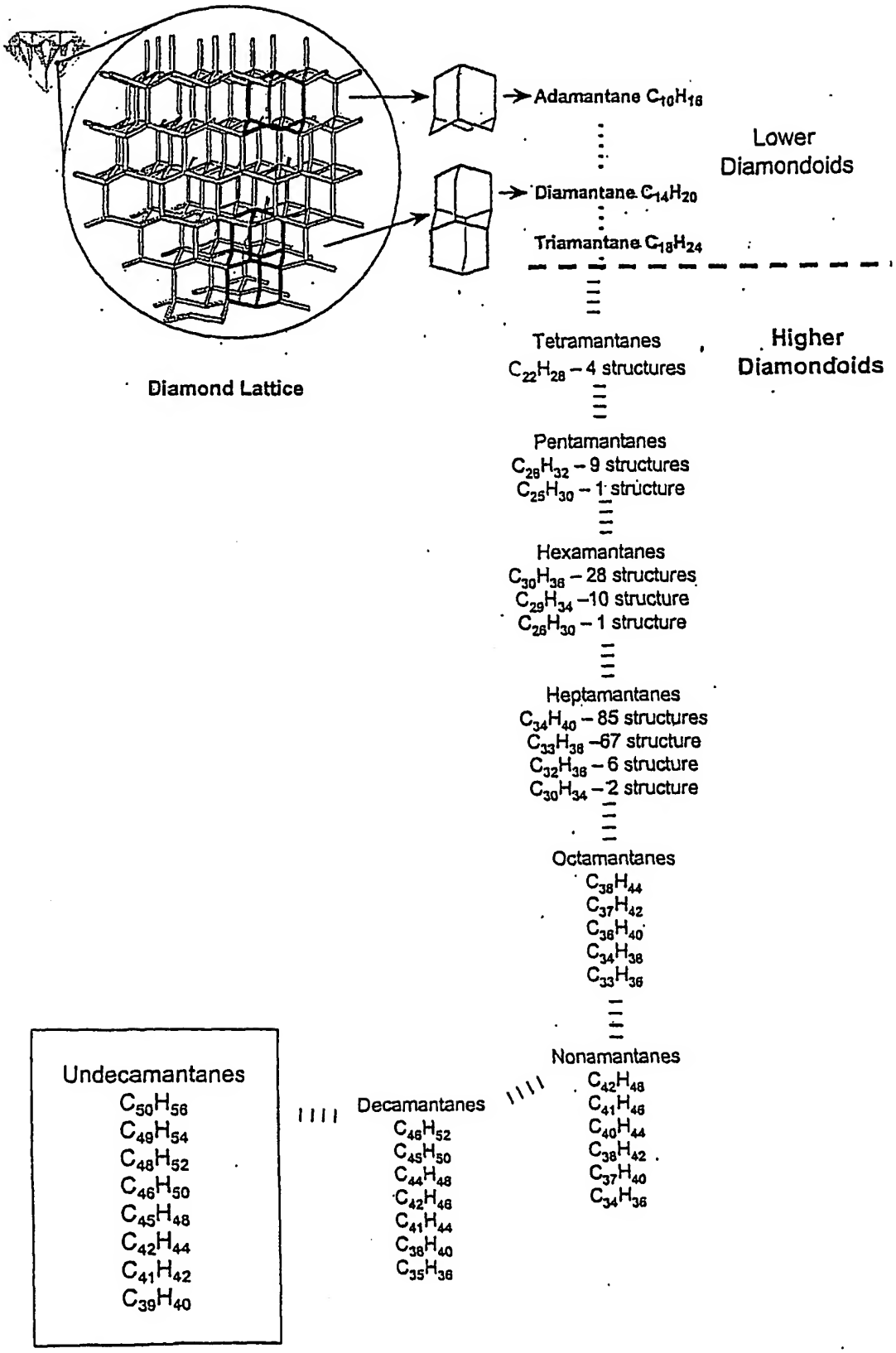

Diamond Lattice
Adamantane $C_{10}H_{16}$
Diamantane $C_{14}H_{20}$
Triamantane $C_{18}H_{24}$
Lower Diamondoids
Higher Diamondoids
Tetramantanes
$C_{22}H_{28}$ – 4 structures
Pentamantanes
$C_{26}H_{32}$ – 9 structures
$C_{25}H_{30}$ – 1 structure
Hexamantanes
$C_{30}H_{36}$ – 28 structures
$C_{29}H_{34}$ –10 structure
$C_{26}H_{30}$ – 1 structure
Heptamantanes
$C_{34}H_{40}$ – 85 structures
$C_{33}H_{38}$ –67 structure
$C_{32}H_{38}$ – 6 structure
$C_{30}H_{34}$ – 2 structure
Octamantanes
$C_{38}H_{44}$
$C_{37}H_{42}$
$C_{36}H_{40}$
$C_{34}H_{38}$
$C_{33}H_{36}$
Nonamantanes
$C_{42}H_{48}$
$C_{41}H_{46}$
$C_{40}H_{44}$
$C_{38}H_{42}$
$C_{37}H_{40}$
$C_{34}H_{36}$
Decamantanes
$C_{46}H_{52}$
$C_{45}H_{50}$
$C_{44}H_{48}$
$C_{42}H_{46}$
$C_{41}H_{44}$
$C_{38}H_{40}$
$C_{35}H_{36}$
Undecamantanes
$C_{50}H_{56}$
$C_{49}H_{54}$
$C_{48}H_{52}$
$C_{46}H_{50}$
$C_{45}H_{48}$
$C_{42}H_{44}$
$C_{41}H_{42}$
$C_{39}H_{40}$

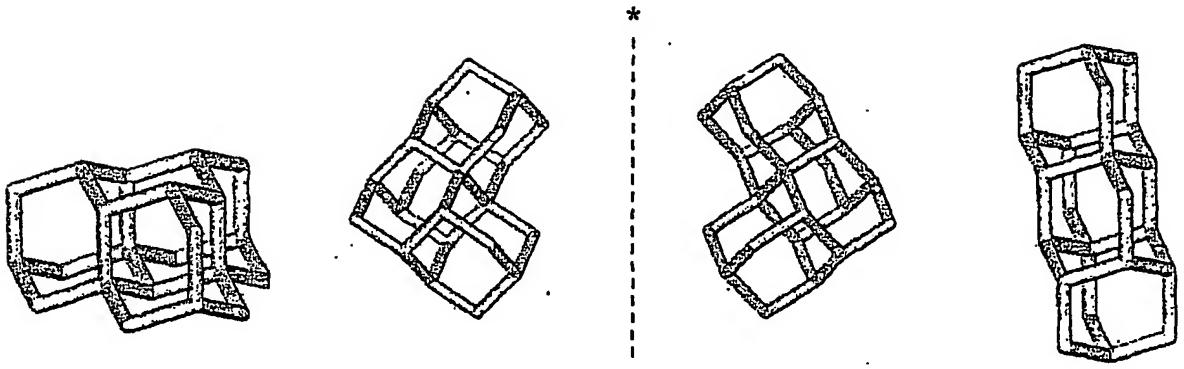
FIG. 2

Number of Diamond Crystal Cage Units	Number of Molecular Formulae	Higher Diamondoid	Molecular Weights							
4	1	Tetramantane	292							
5	2	Pentamantane	344	330						
6	3	Hexamantane	396	382	342					
7	4	Heptamantane	448	434	394	420				
8	5	Octamantane	500	486	446	472	432			
9	6	Nonamantane	552	538	498	524	484	444		
10	7	Decamantane	604	590	550	576	536	496	456	
11	8	Undecamantane	656	642	602	628	588	548	508	534

Most Preferred
Preferred

FIG. 3

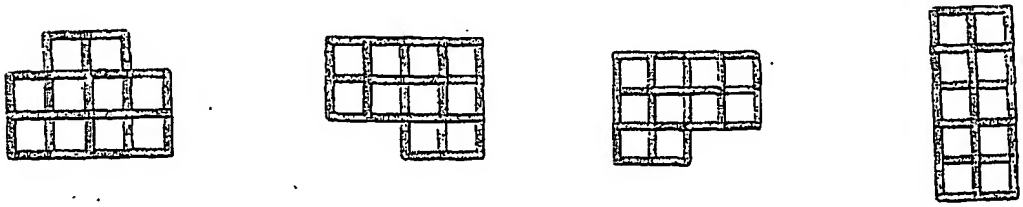
Tetramantanes



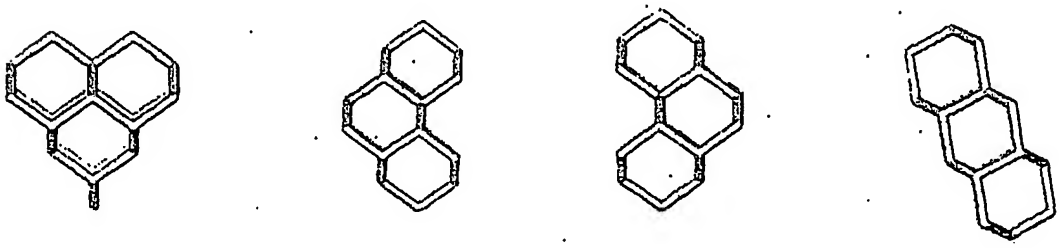
[1(2)3] [123] Enantiomer B [123] Enantiomer A [121]

FIG. 4

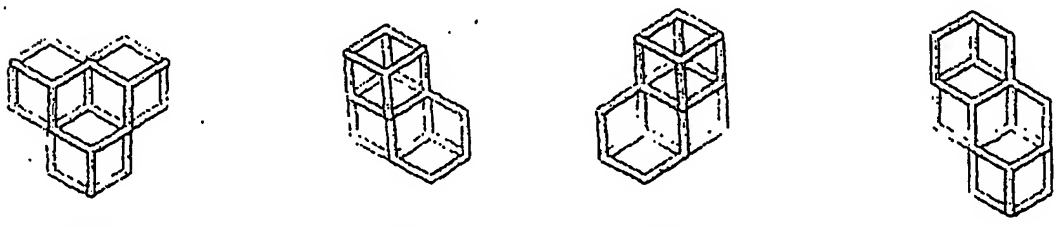
A Tetramantanes – view into the Corresponding Diamond 100



B Tetramantanes – view into the Corresponding Diamond 110



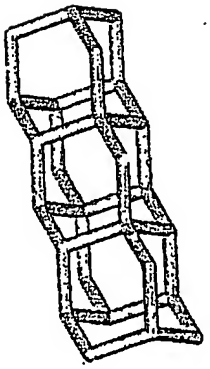
C Tetramantanes – view into the Corresponding Diamond 111



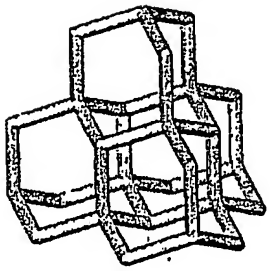
[1(2)3] [123] Enantiomer B [123] Enantiomer A [121]

FIG. 5

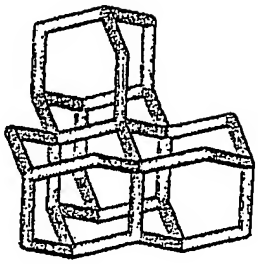
Pentamantanes



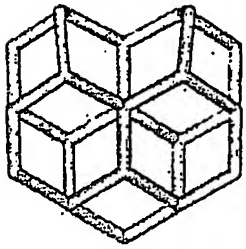
[1212]



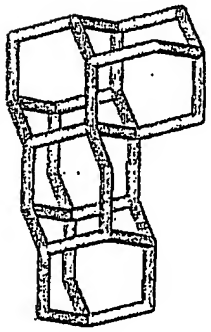
[1(2,3)4]



[12(3)4]

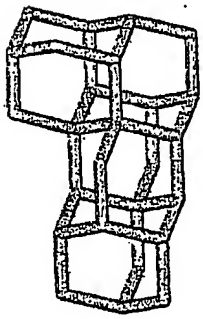


[1231]

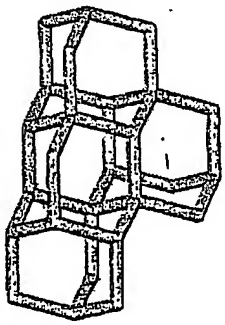


[1213]
Enantiomer A

*

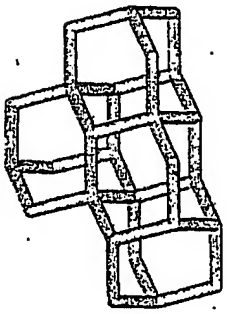


[1213]
Enantiomer B

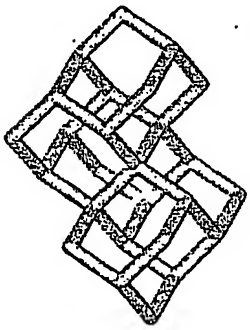


[12(1)3]
Enantiomer B

*

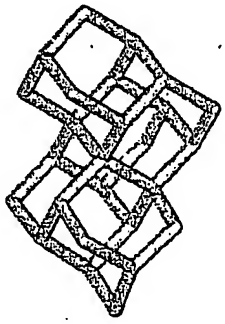


[12(1)3]
Enantiomer A



[1234]
Enantiomer A

*

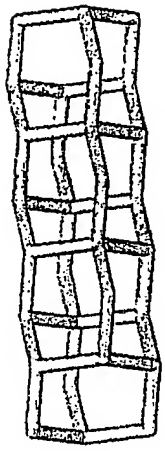


[1234]
Enantiomer B

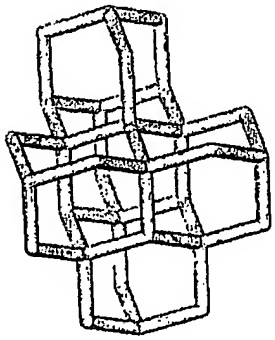
* Indicated mirror plane

FIG. 6A

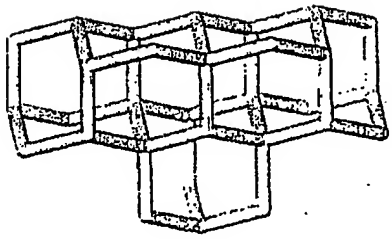
Hexamantanes
(Achiral)



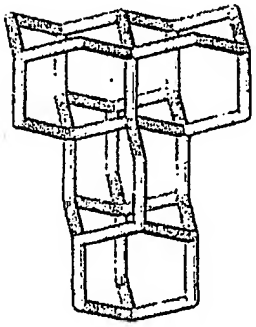
[12121]



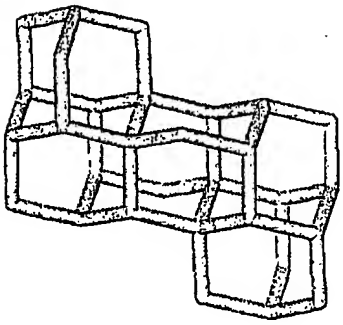
[12(1,3)4]



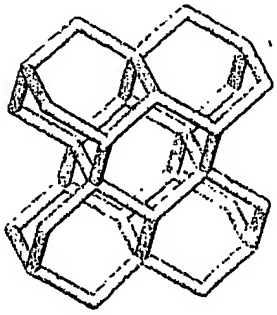
[12(3)12]



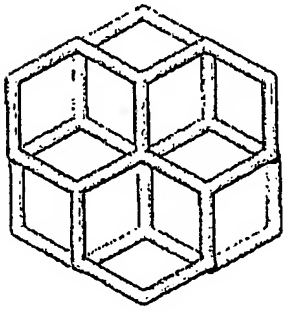
[121(3)4]



[12321]



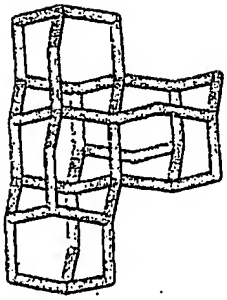
[1(2)3(1)2]



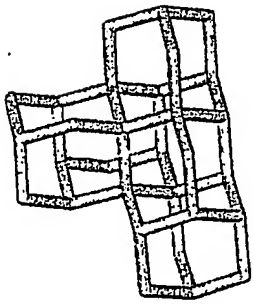
[12312]

FIG. 6B

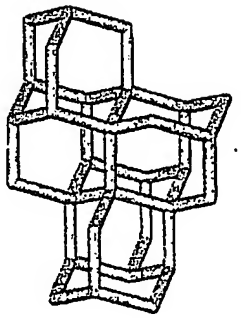
Hexamantanes
(Chiral)



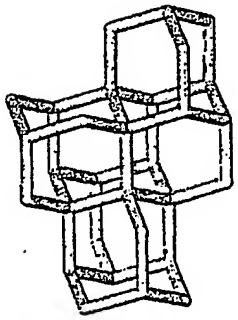
[12(1)32]
Enantiomer A



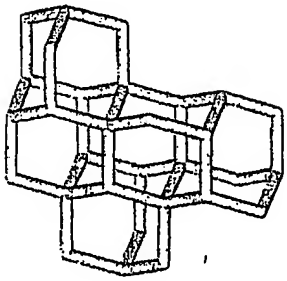
[12(1)32]
Enantiomer B



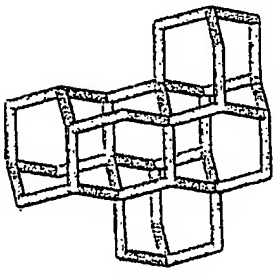
[12(3)14]
Enantiomer A



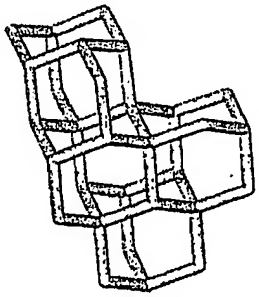
[12(3)14]
Enantiomer B



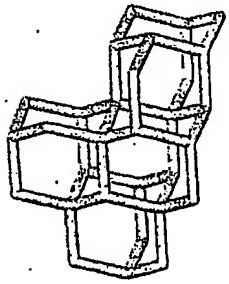
[12(1)34]
Enantiomer B



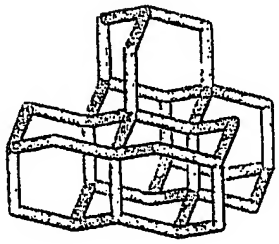
[12(1)34]
Enantiomer A



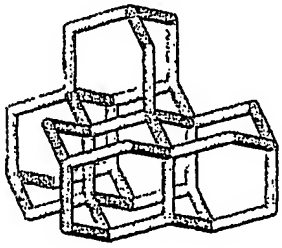
[1(2)314]
Enantiomer B



[1(2)314]
Enantiomer A



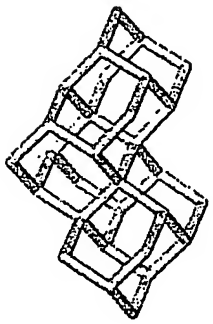
[[1(2)3(1)4]
Enantiomer A



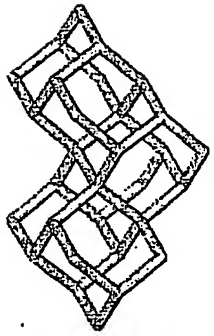
[[1(2)3(1)4]
Enantiomer B

FIG. 6C

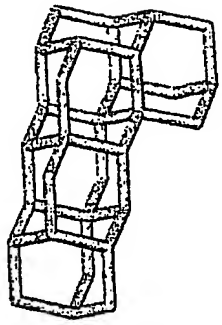
Hexamantanes
(Chiral)



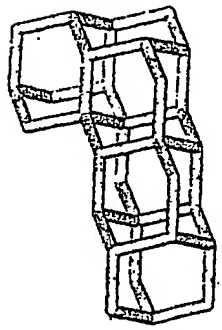
[12341]
Enantiomer A



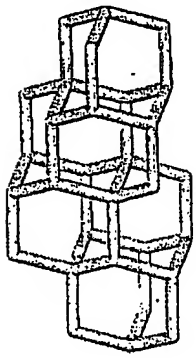
[12341]
Enantiomer B



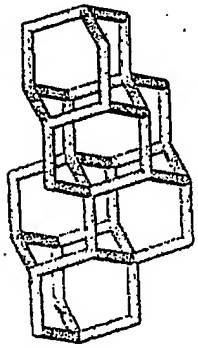
[12123]
Enantiomer B



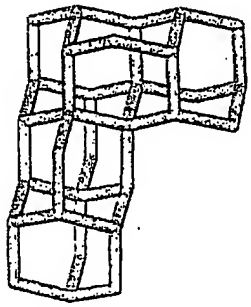
[12123]
Enantiomer A



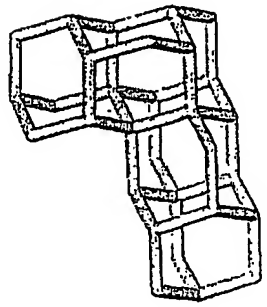
[12131]
Enantiomer A



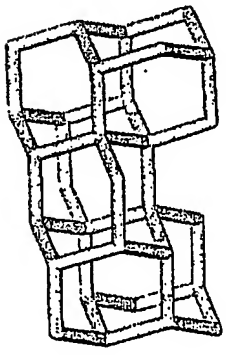
[12131]
Enantiomer B



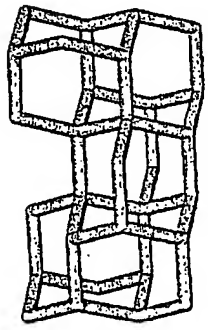
[12134]
Enantiomer A



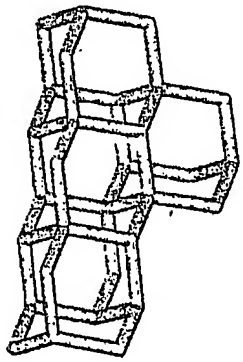
[12134]
Enantiomer B



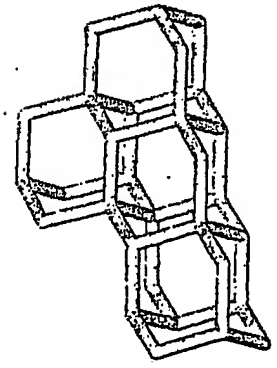
[12324]
Enantiomer A



[12324]
Enantiomer B



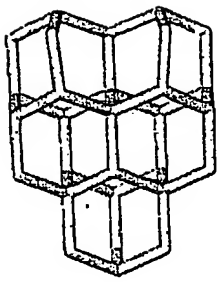
[121(2)3]
Enantiomer A



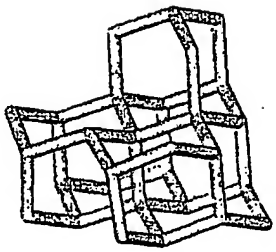
[121(2)3]
Enantiomer B

FIG. 6D

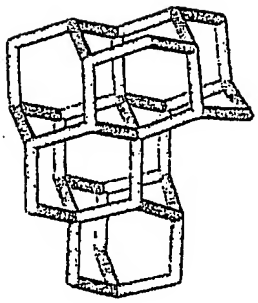
Hexamantanes
382 Mol. Wt.



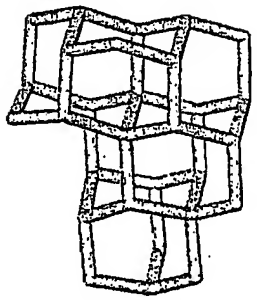
[12(1)31]



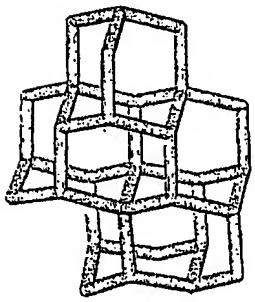
[12(3)41]



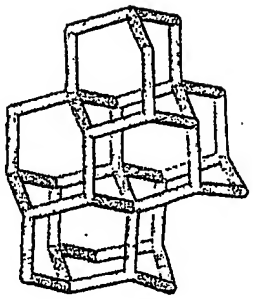
[12132]
Enantiomer A



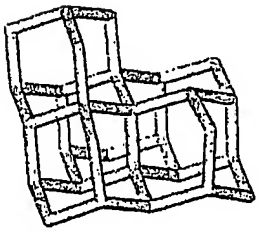
[12132]
Enantiomer B



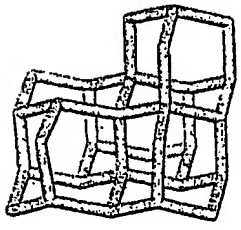
[123(1)2]
Enantiomer A



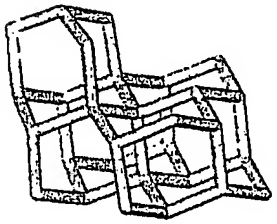
[123(1)2]
Enantiomer B



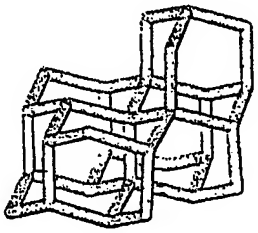
[123(1)4]
Enantiomer A



[123(1)4]
Enantiomer B

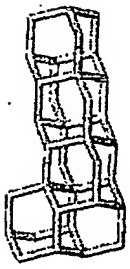


[12314]
Enantiomer A

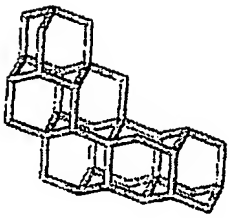


[12314]
Enantiomer B

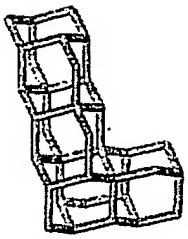
FIG. 7A



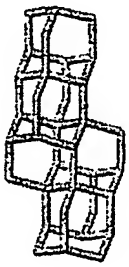
121213



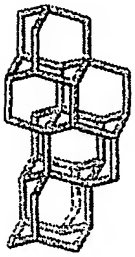
121232



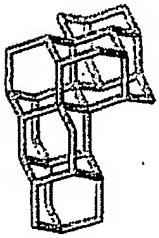
121234



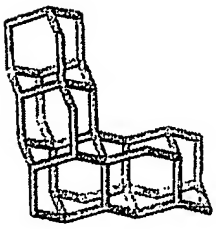
121312



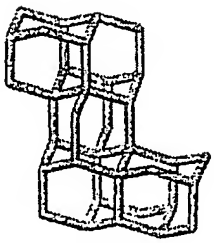
121314



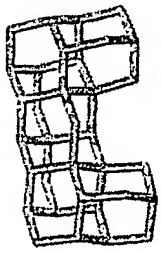
121342



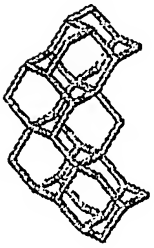
121343



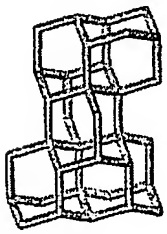
123214



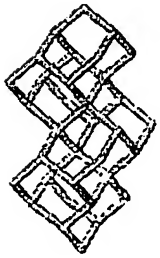
123231



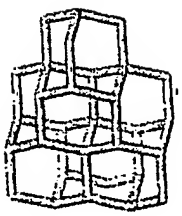
123234



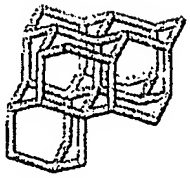
123241



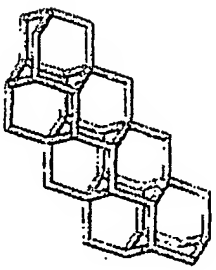
123412



121321



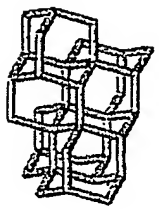
123124



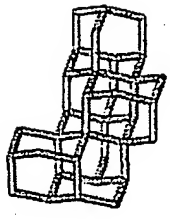
121212

No 10/98 available - GT

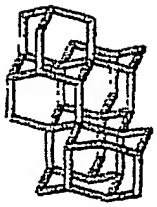
FIG. 7C



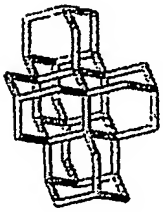
12(3)1(3)4



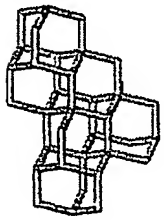
12(3)124



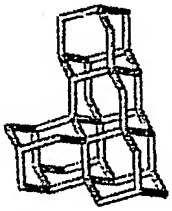
12(3)134



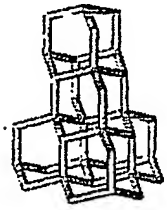
12(3,4)12



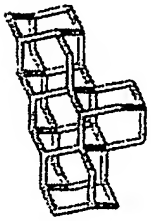
121(2)31



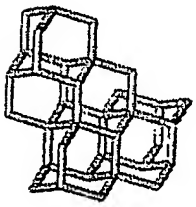
121(2)34



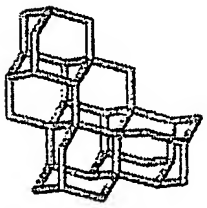
121(2,3)4



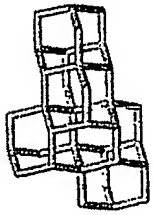
121(3)21



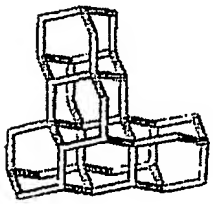
121(3)23



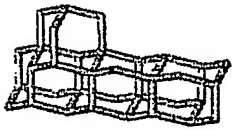
121(3)24



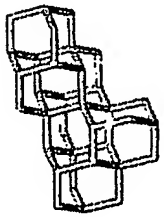
121(3)41



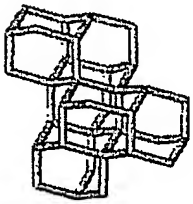
121(3)43



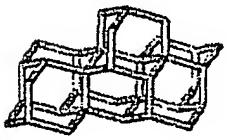
1212(1)3



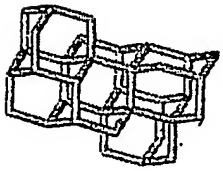
1213(1)4



123(2)41

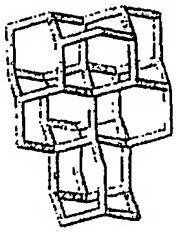


123(4)21

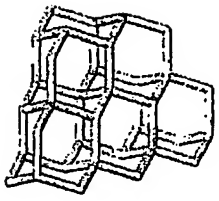


1232(1)4

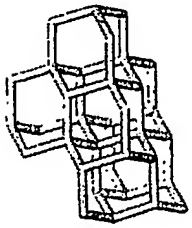
FIG. 8



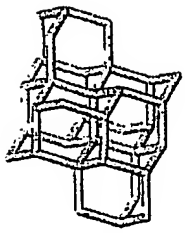
[1232432]



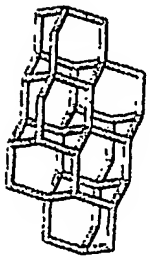
[12132(1)3]



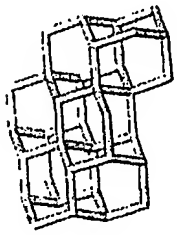
[123(2,4)12]



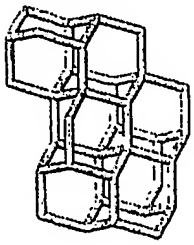
[1234(1)23]



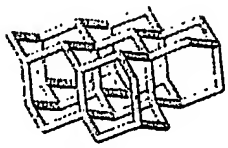
[1213(1)21]



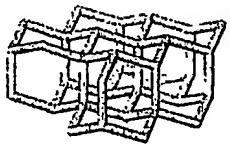
[1212312] A



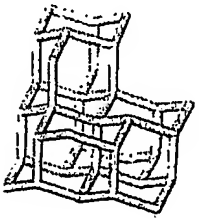
[1212312] B



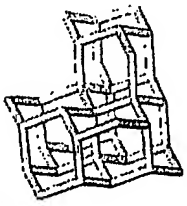
[1213212] A



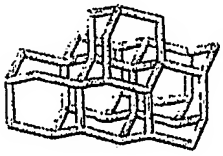
[1213212] B



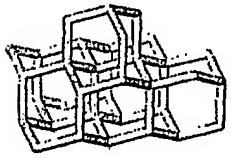
[1213413] A



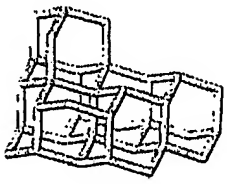
[1213413] B



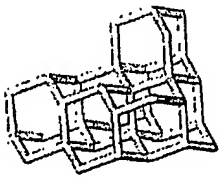
[1213214] A



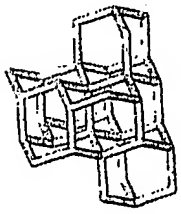
[1213214] B



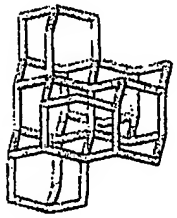
[12132(1)4] A



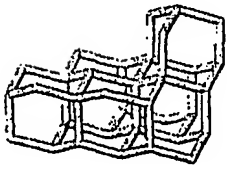
[12132(1)4] B



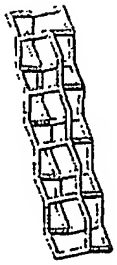
[1234231 A



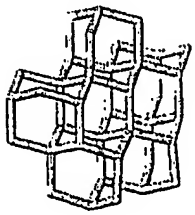
[1234231 B



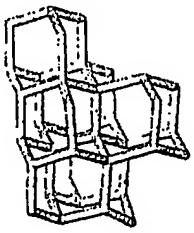
[1213(4)21]



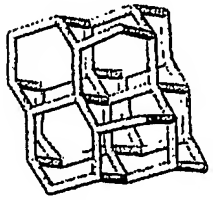
[1212121]
500 mol. wt.



[1(2)3(4)1(2)3]
486 mol. wt.

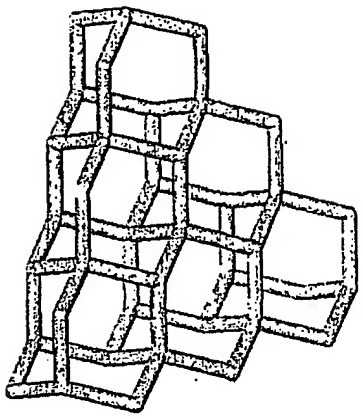


[1232142]
472 mol. wt.

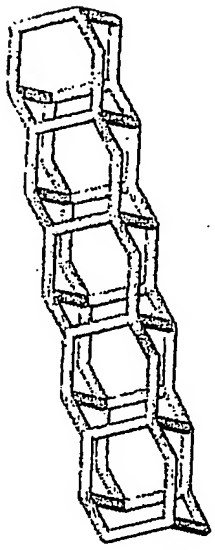


[12342(1)]
432 mol. wt.

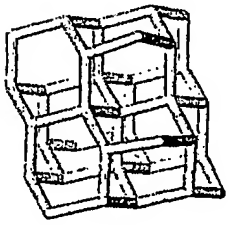
FIG. 9



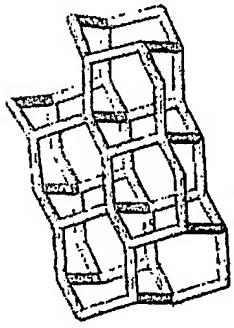
[121(2)32(1)3]
498 molecular weight



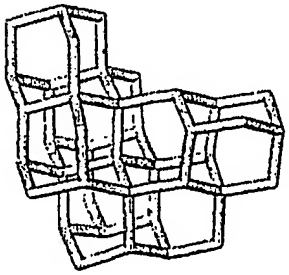
[12121212] nonamantane
552 molecular weight



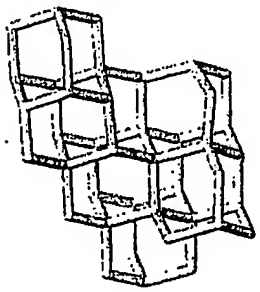
A 444 molecular weight
nonamantane



A 484 molecular weight
nonamantane

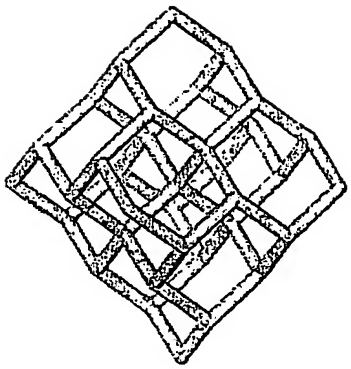


A 524 molecular weight
nonamantane

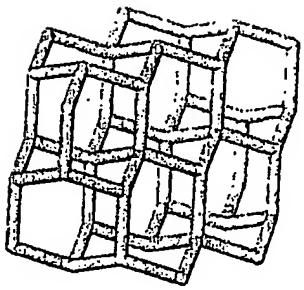


A 538 molecular weight
nonamantane

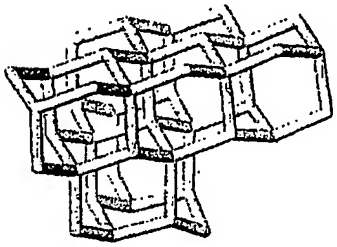
FIG. 10



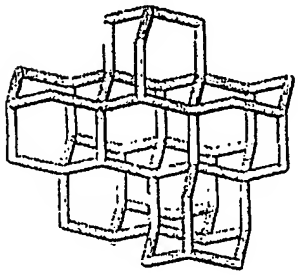
[1231241(2)3]
456 mol. wt.



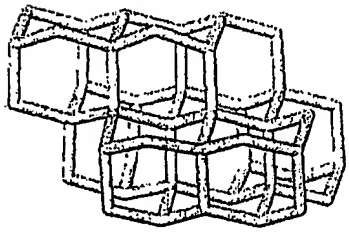
[121231212]
496 mol. wt.



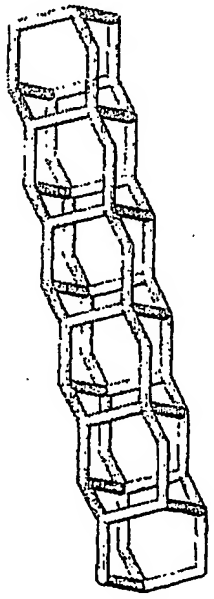
[121(2)32431]
536 mol. wt.



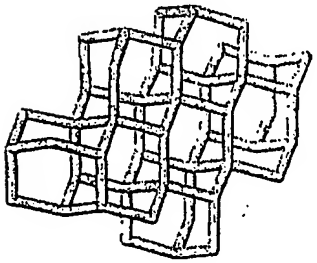
[1213(4)2(3)12]
550 mol. wt.



[121324(2)34]
576 mol. wt.

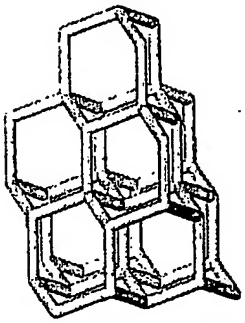


[121212121]
604 mol. wt.

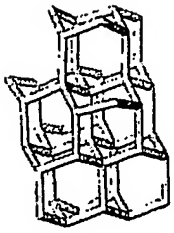


[12(3)1(4)2(3)12]
590 mol. wt.

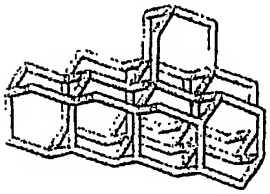
FIG. 11



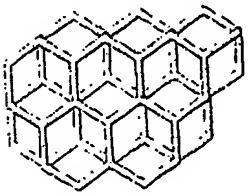
[123(1,2)42143] undecamantane



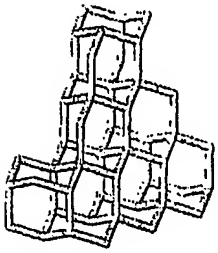
A 534 molecular weight



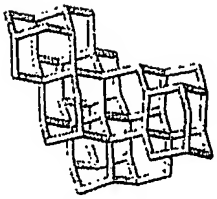
A 588 molecular weight



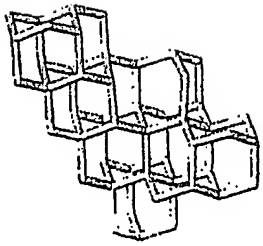
A 548 molecular weight



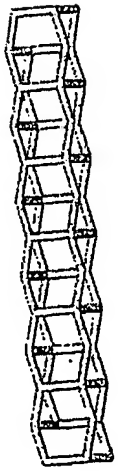
A 602 molecular weight



A 628 molecular weight



A 642 molecular weight



A 656 molecular weight

FIG. 12

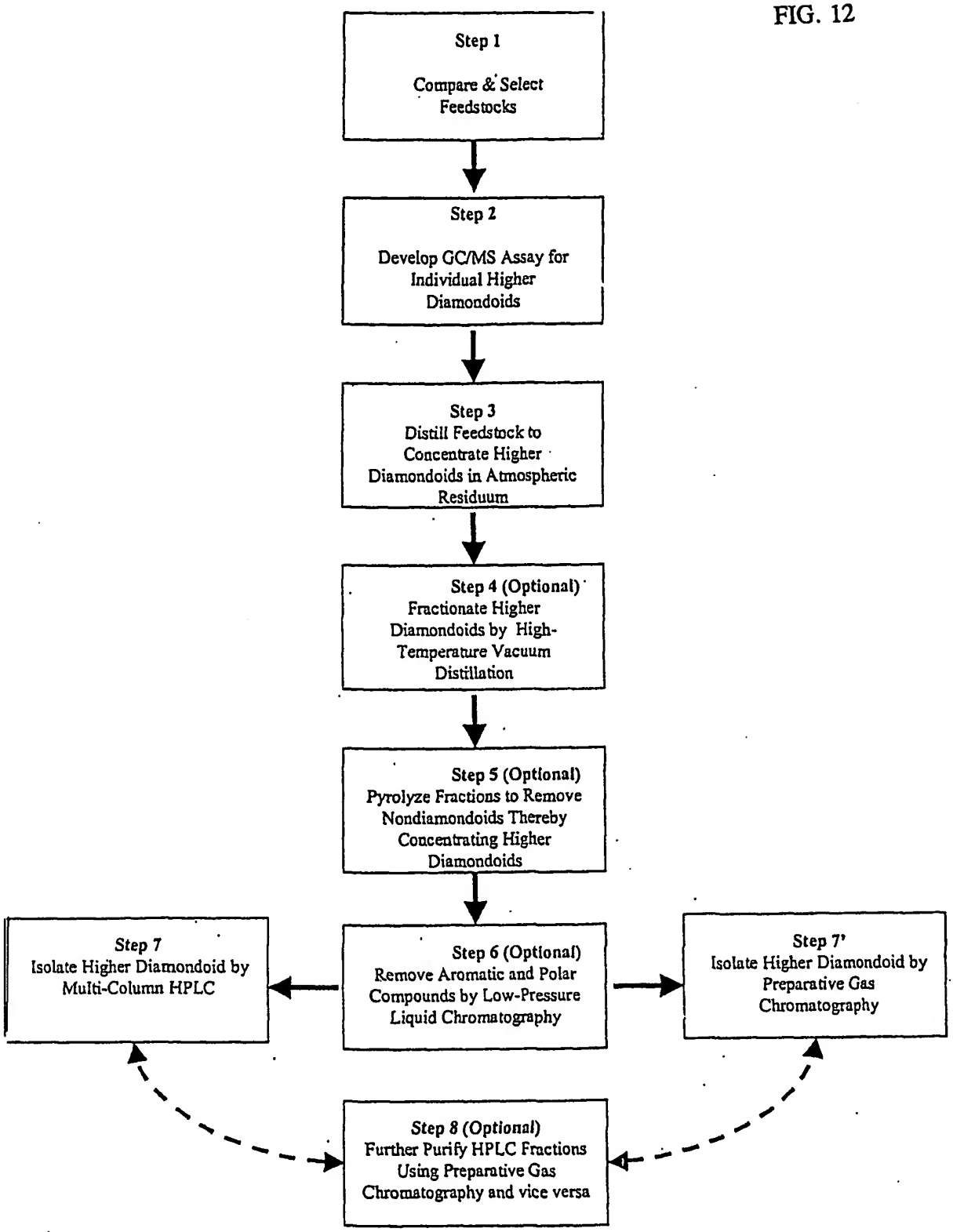

Step 1
Compare & Select Feedstocks
Step 2
Develop GC/MS Assay for Individual Higher Diamondoids
Step 3
Distill Feedstock to Concentrate Higher Diamondoids in Atmospheric Residuum
Step 4 (Optional)
Fractionate Higher Diamondoids by High-Temperature Vacuum Distillation
Step 5 (Optional)
Pyrolyze Fractions to Remove Nondiamondoids Thereby Concentrating Higher Diamondoids
Step 6 (Optional)
Remove Aromatic and Polar Compounds by Low-Pressure Liquid Chromatography
Step 7
Isolate Higher Diamondoid by Multi-Column HPLC
Step 7'
Isolate Higher Diamondoid by Preparative Gas Chromatography
Step 8 (Optional)
Further Purify HPLC Fractions Using Preparative Gas Chromatography and vice versa

FIG. 13A

Higher Diamondoid	Compound Reference Number	M+ (m/z) (Equals Base Peak)	GC/MS Retention Times* (min.)	GC/MS Relative Retention Times** (min.)
Tetramantane #1	4-1	292	8.10	1.00
Tetramantane #2	4-2	292	8.66	1.07
Tetramantane #3	4-3	292	9.12	1.13
Pentamantane #1	5-1	344	10.40	1.28
Pentamantane #2	5-2	344	11.93	1.47
Pentamantane #3	5-3	344	11.98	1.48
Pentamantane #4	5-4	344	12.38	1.53
Pentamantane #5	5-5	344	12.50	1.54
Pentamantane #6	5-6	344	12.71	1.57
Cyclohexamantane	C-6	342	12.34	1.52
Hexamantane #1	6-1	396	14.46	1.78
Hexamantane #2	6-2	396	14.61	1.80
Hexamantane #3	6-3	396	14.97	1.85
Hexamantane #4	6-4	396	14.99	1.85
Hexamantane #5	6-5	396	15.04	1.86
Hexamantane #6	6-6	396	15.13	1.87
Hexamantane #7	6-7	396	15.22	1.88
Hexamantane #8	6-8	396	15.32	1.89
Hexamantane #9	6-9	396	15.42	1.90
Hexamantane #10	6-10	396	15.45	1.91
Hexamantane #11	6-11	396	15.49	1.91
Hexamantane #12	6-12	396	15.54	1.92
Hexamantane #13	6-13	396	15.60	1.93
Hexamantane #14	6-14	396	15.81	1.95
Hexamantane #15	6-15	396	15.89	1.96
Hexamantane #16	6-16	396	16.05	1.98
Hexamantane #17	6-17	396	16.08	1.99
Heptamantane #1	7-1	394	14.96	1.85
Heptamantane #2	7-2	394	15.53	1.92
Heptamantane #3	7-3	448	17.34	2.14
Heptamantane #4A	7-4A	448	17.70	2.18
Heptamantane #4B	7-4B	448	17.70	2.18
Heptamantane #5	7-5	448	17.71	2.19
Heptamantane #6	7-6	448	17.79	2.20
Heptamantane #7	7-7	448	17.82	2.20
Heptamantane #8	7-8	448	17.99	2.22
Heptamantane #9A	7-9A	448	18.13	2.24
Heptamantane #9B	7-9B	448	18.13	2.24
Heptamantane #9C	7-9C	448	18.13	2.24
Heptamantane #10	7-10	448	18.15	2.24
Heptamantane #11	7-11	448	18.20	2.25
Heptamantane #12	7-12	448	18.21	2.25
Heptamantane #13A	7-13A	448	18.29	2.26
Heptamantane #13B	7-13B	448	18.29	2.26
Heptamantane #13C	7-13C	448	18.29	2.26
Heptamantane #14	7-14	448	18.32	2.26

FIG. 13A, continued

Higher Diamondoid	Compound Reference Number	M+ (m/z) (Equals Base Peak)	GC/MS Retention Times* (min.)	GC/MS Relative Retention Times** (min.)
Octamantane #1	8-1	446	17.30	2.14
Octamantane #2	8-2	446	17.37	2.14
Octamantane #3	8-3	446	17.42	2.15
Octamantane #4	8-4	446	17.47	2.16
Octamantane #5	8-5	446	17.71	2.19
Octamantane #6	8-6	446	17.82	2.20
Octamantane #7	8-7	446	17.86	2.20
Octamantane #8	8-8	446	18.22	2.25
Octamantane #9	8-9	446	18.46	2.28
Octamantane #10	8-10	446	18.65	2.30
Octamantane #11	8-11	446	18.76	2.32
Nonamantane #1	9-1	498	19.86	2.45
Decamantane #1	10-1	456	18.57	2.29
Decamantane #2	10-2	496	21.33	2.63
Undecamantane#1	11-1	508	21.05	2.60

* HP-MS5 (30m X 0.25 mm, 0.25 micron film), helium carrier gas,
** Reference to Tetramantane #1

FIG. 13B

Higher Diamondoid	Compound Reference Number	Fraction Number	Elution Time (min.)	Elution Volume (mL)	Elution Volume Relative to 4-1
Tetramantane #1	4-1	4	119	594	1.00
Tetramantane #2	4-2	7	125	627	1.05
Tetramantane #3	4-3	6	123	616	1.04
Pentamantane #1	5-1	11	134	669	1.13
Pentamantane #2	5-2	19	151	754	1.27
Pentamantane #3	5-3	28	170	850	1.43
Pentamantane #4	5-4	22	157	786	1.32
Pentamantane #5	5-5	19	151	754	1.27
Pentamantane #6	5-6	20	153	765	1.29
Cyclohexamantane	C-6	23	159	797	1.34
Hexamantane #1	6-1	33	181	903	1.52
Hexamantane #2	6-2	29	172	861	1.45
Hexamantane #3	6-3	43	202	1012	1.70
Hexamantane #4	6-4	33	181	903	1.52
Hexamantane #5	6-5	35	185	924	1.56
Hexamantane #6	6-6	63	242	1211	2.04
Hexamantane #7	6-7	37	189	945	1.59
Hexamantane #8	6-8	39	193	967	1.63
Hexamantane #9	6-9	39	193	967	1.63
Hexamantane #10	6-10	48	214	1071	1.80
Hexamantane #11	6-11	36	187	935	1.57
Hexamantane #12	6-12	44	205	1024	1.72
Hexamantane #13	6-13	36	187	935	1.57
Hexamantane #14	6-14	39	193	967	1.63
Hexamantane #15	6-15	45	207	1036	1.74
Hexamantane #16	6-16	44	205	1024	1.72
Hexamantane #17	6-17	49	217	1083	1.82
Heptamantane #1	7-1	45	207	1036	1.74
Heptamantane #2	7-2	41	198	989	1.66
Heptamantane #3	7-3	61	238	1190	2.00
Heptamantane #4A	7-4A	90	304	1519	2.56
Heptamantane #4B	7-4B	90	304	1519	2.56
Heptamantane #5	7-5	76	270	1349	2.27
Heptamantane #6	7-6	67	251	1253	2.11
Heptamantane #7	7-7	—	—	—	—
Heptamantane #8	7-8	59	234	1172	1.97
Heptamantane #9A	7-9A	60	236	1181	1.99
Heptamantane #9B	7-9B	62	240	1200	2.02
Heptamantane #9C	7-9C	78	274	1370	2.31
Heptamantane #10	7-10	86	291	1455	2.45
Heptamantane #11	7-11	—	—	—	—
Heptamantane #12	7-12	—	—	—	—
Heptamantane #13A	7-13A	58	233	1163	1.96
Heptamantane #13B	7-13B	74	266	1328	2.24
Heptamantane #13C	7-13C	90	304	1519	2.56
Heptamantane #14	7-14	70	257	1285	2.16

FIG. 13B, continued

Higher Diamondoid	Compound Reference Number	Fraction Number	Elution Time (min.)	Elution Volume (mL)	Elution Volume Relative to 4-1
Octamantane #1	8-1	81	280	1402	2.36
Octamantane #2	8-2	83	285	1423	2.40
Octamantane #3	8-3	64	244	1221	2.06
Octamantane #4	8-4	—	—	—	—
Octamantane #5	8-5	63	242	1211	2.04
Octamantane #6	8-6	79	276	1381	2.32
Octamantane #7	8-7	71	259	1296	2.18
Octamantane #8	8-8	84	287	1434	2.41
Octamantane #9	8-9	74	266	1328	2.24
Octamantane #10	8-10	80	280	1402	2.36
Octamantane #11	8-11	85	289	1445	2.43
Nonamantane #1	9-1	89	297	1487	2.50
Decamantane #1	10-1	83	285	1423	2.40
Decamantane #2	10-2	—	—	—	—
Undecamantane#1	11-1	101	355	1774	2.99

ODS HPLC Whatman ODS-II 10/50
(2 Columns in series), acetone mobile phase @5.0 mL/min.

FIG. 14

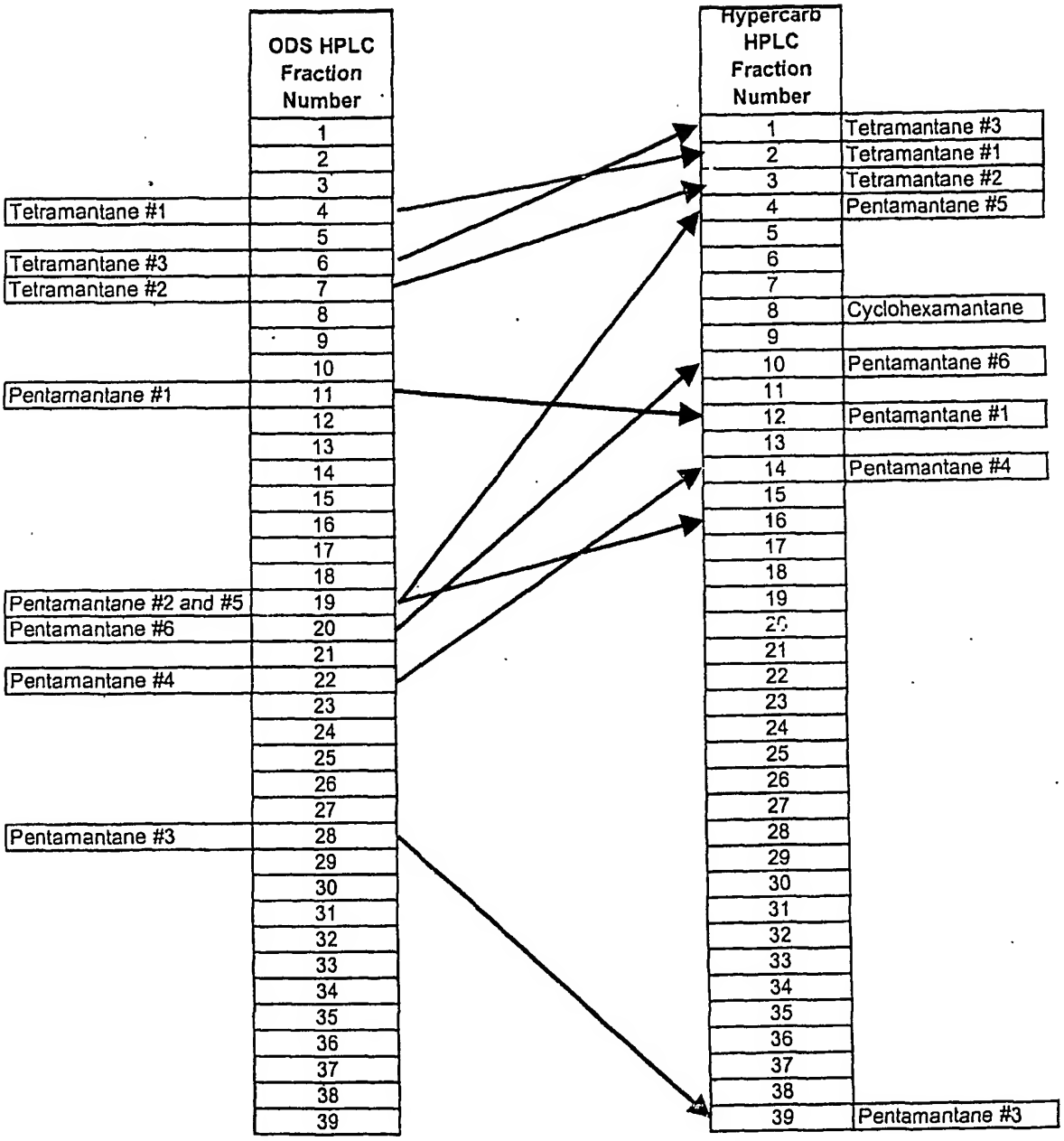

ODS HPLC Fraction Number
Hypercarb HPLC Fraction Number
Tetramantane #1
Tetramantane #3
Tetramantane #2
Pentamantane #1
Pentamantane #2 and #5
Pentamantane #6
Pentamantane #4
Pentamantane #3
Tetramantane #3
Tetramantane #1
Tetramantane #2
Pentamantane #5
Cyclohexamantane
Pentamantane #6
Pentamantane #1
Pentamantane #4
Pentamantane #3

FIG. 15

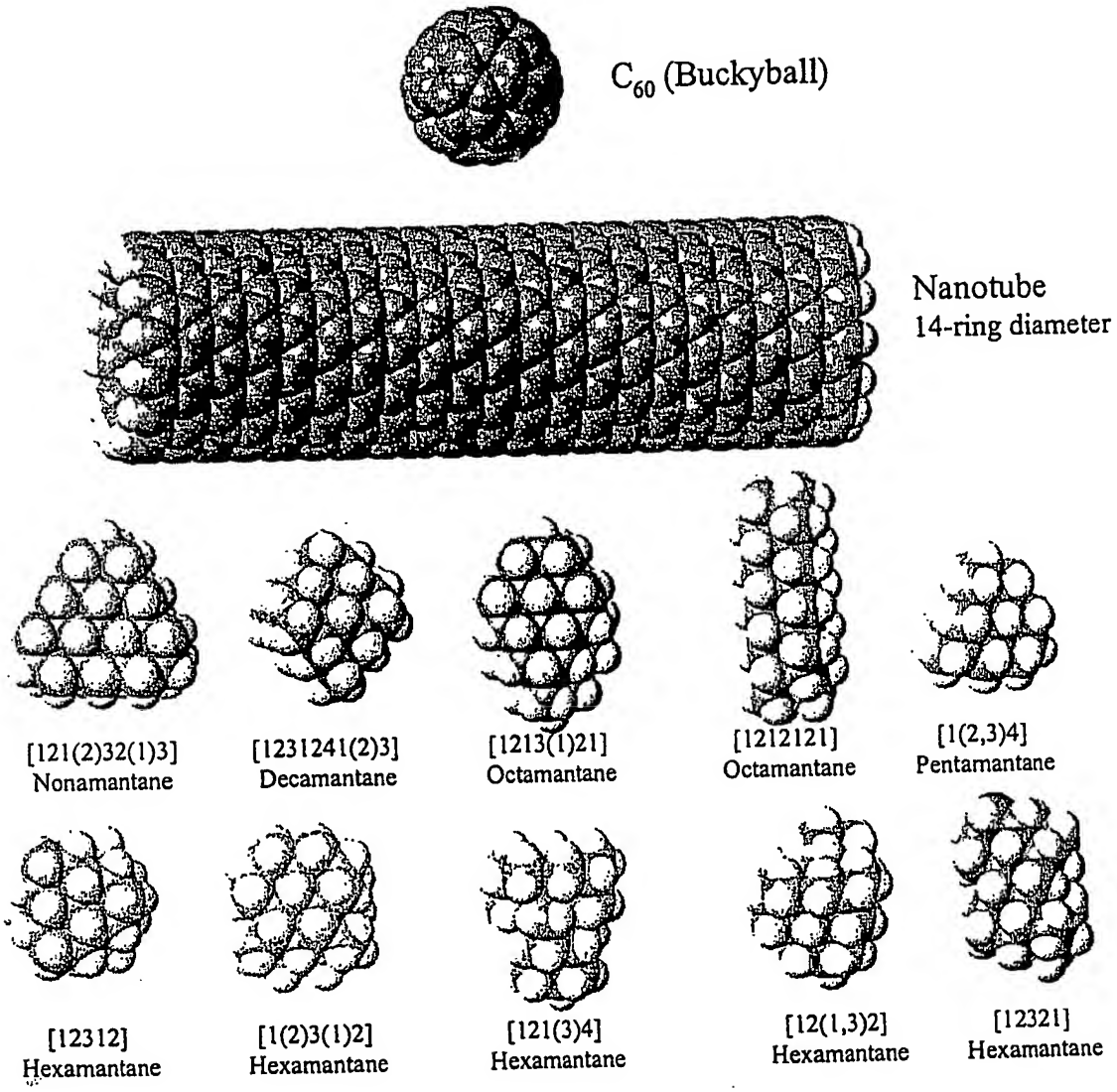

C_{60} (Buckyball)
Nanotube
14-ring diameter
[121(2)32(1)3]
Nonamantane
[1231241(2)3]
Decamantane
[1213(1)21]
Octamantane
[1212121]
Octamantane
[1(2,3)4]
Pentamantane
[12312]
Hexamantane
[1(2)3(1)2]
Hexamantane
[121(3)4]
Hexamantane
[12(1,3)2]
Hexamantane
[12321]
Hexamantane

FIG. 16

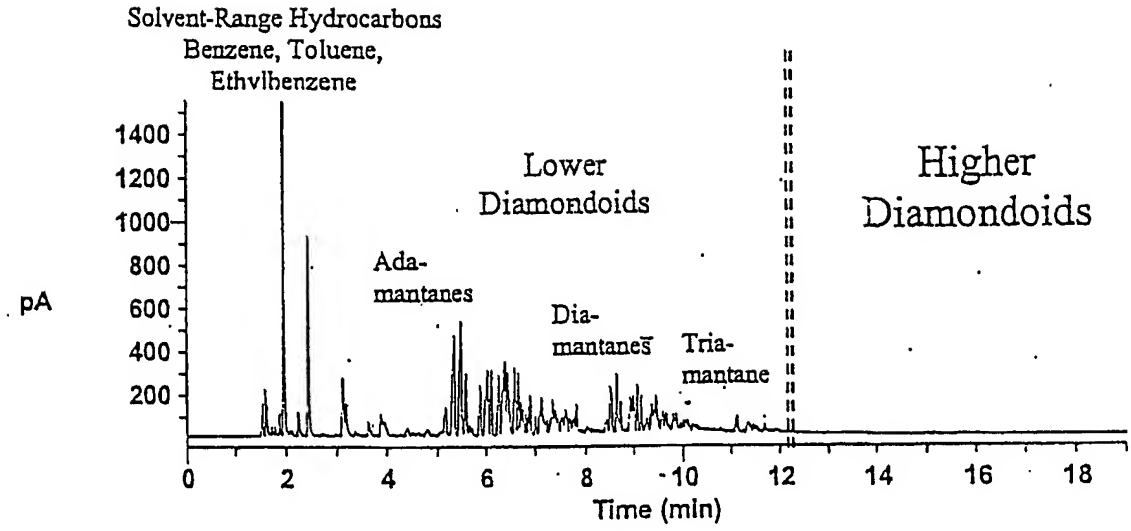

Solvent-Range Hydrocarbons
Benzene, Toluene,
Ethylbenzene
Lower
Diamondoids
Higher
Diamondoids
Ada-
mantanes
Dia-
mantanes
Tria-
mantane
pA
1400
1200
1000
800
600
400
200
0
2
4
6
8
10
12
14
16
18
Time (min)

FIG. 17

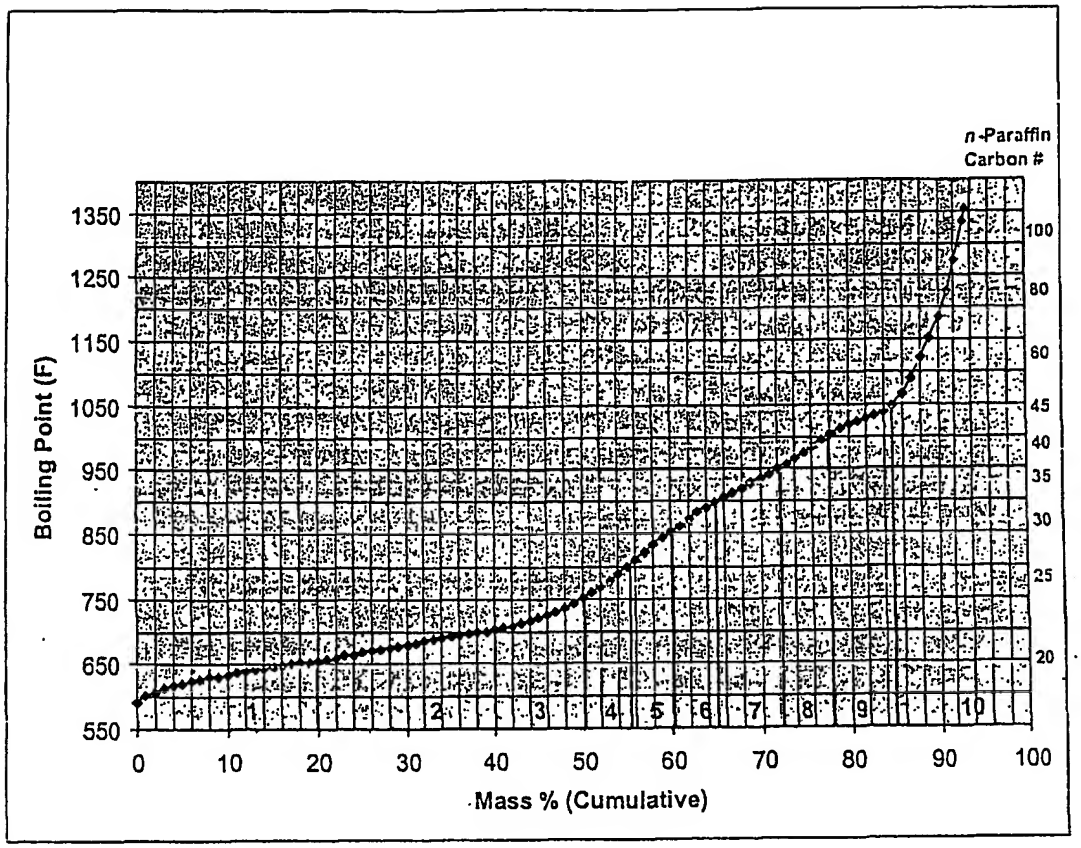

n-Paraffin Carbon #
Boiling Point (F)
1350
1250
1150
1050
950
850
750
650
550
100
80
60
45
40
35
30
25
20
1
2
3
4
5
6
7
8
9
10
0
10
20
30
40
50
60
70
80
90
100
Mass % (Cumulative)

FIG. 18A

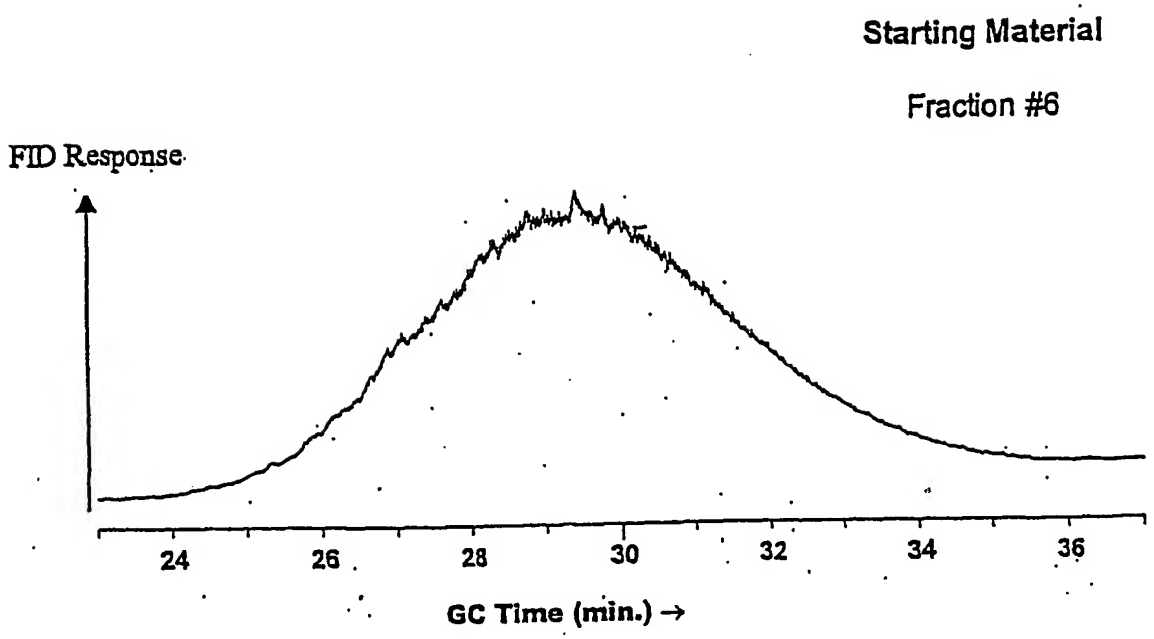


FIG. 18B

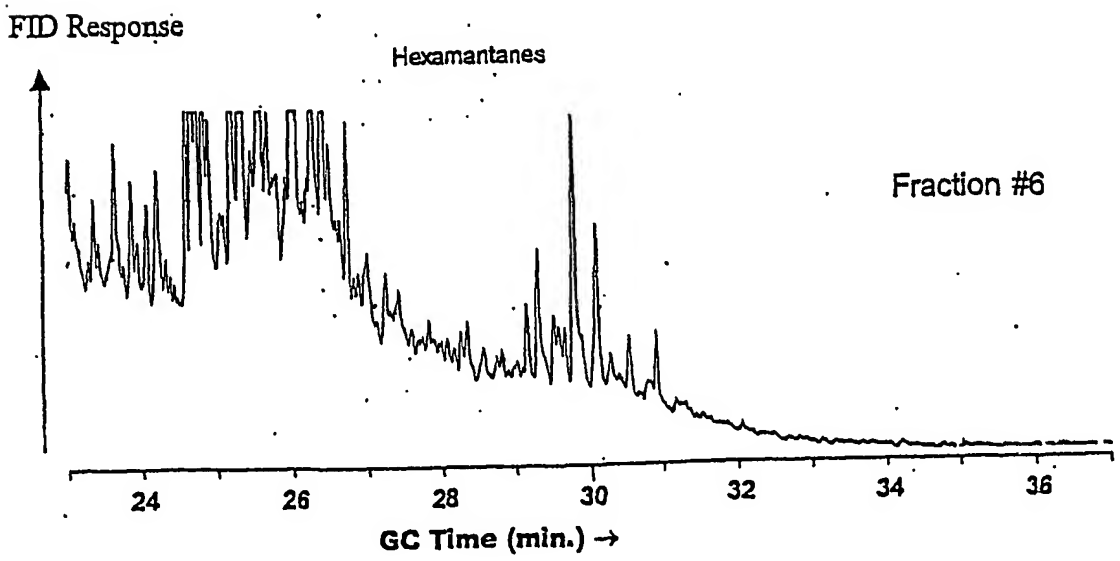


FIG. 19

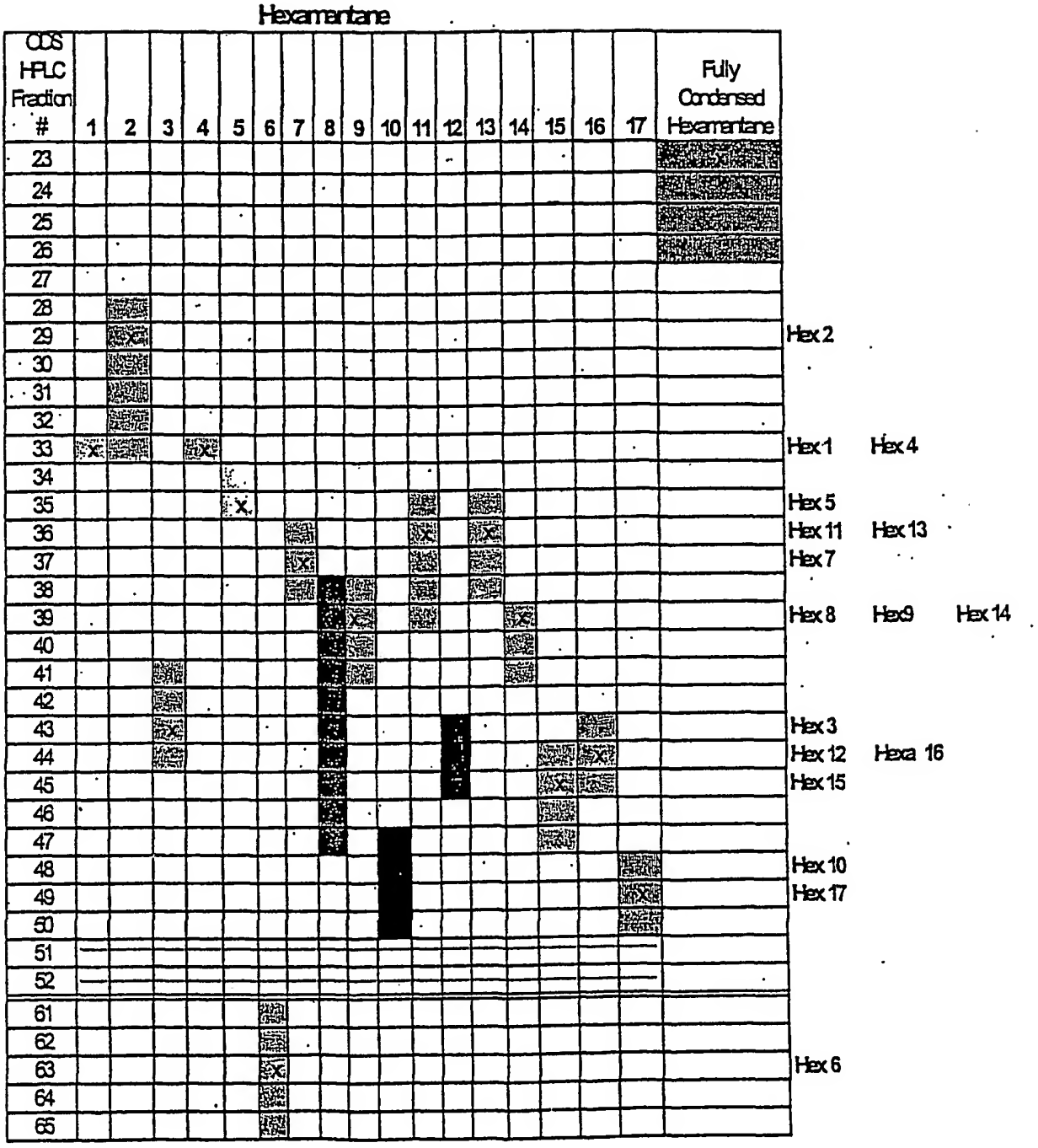

Hexamantane
COS HPLC Fraction #
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
Fully Condensed Hexamantane
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
61
62
63
64
65
Hex 2
Hex 1
Hex 4
Hex 5
Hex 11
Hex 13
Hex 7
Hex 8
Hex9
Hex 14
Hex 3
Hex 12
Hexa 16
Hex 15
Hex 10
Hex 17
Hex 6

FIG. 20

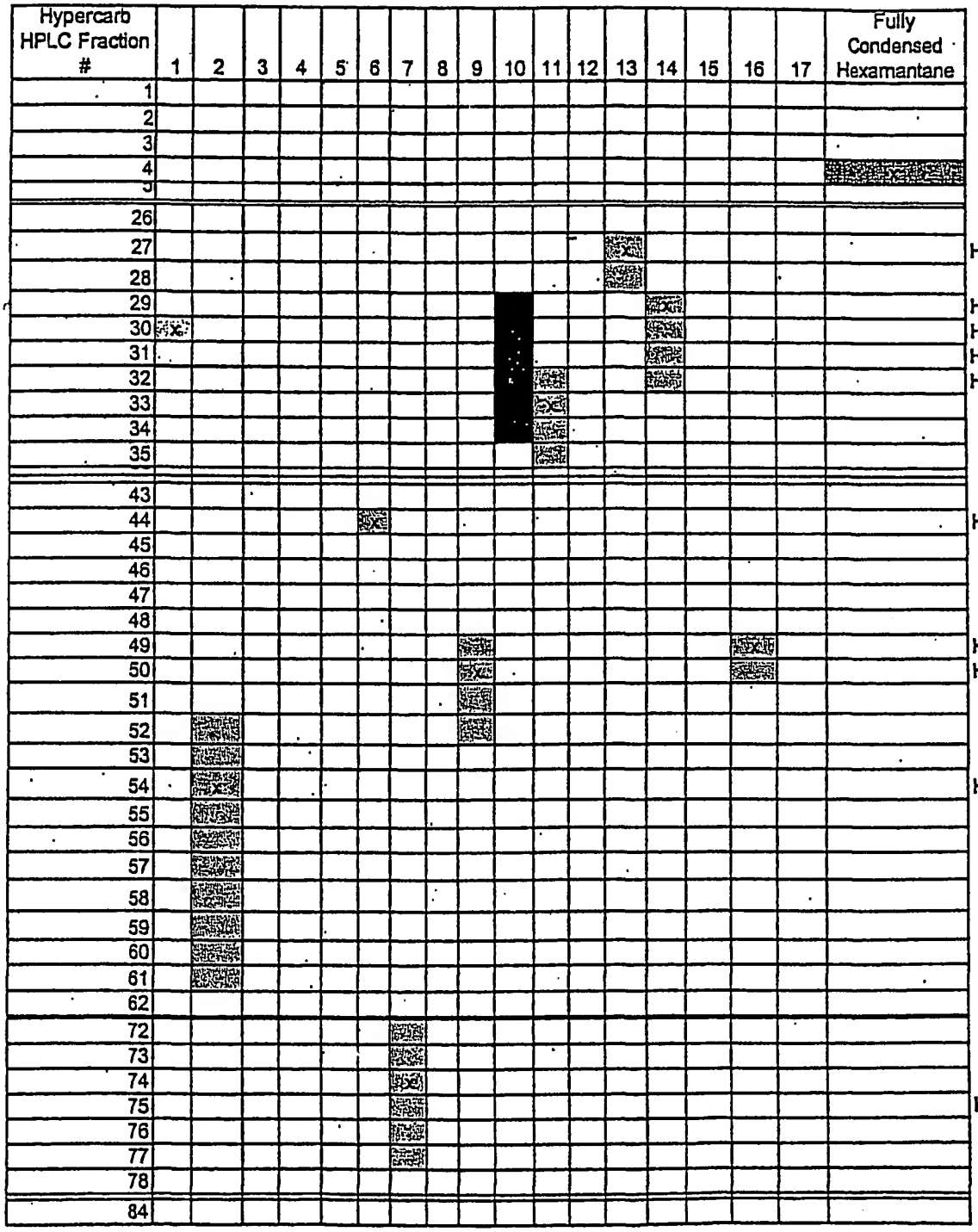

Hypercarb HPLC Fraction #
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
Fully Condensed Hexamantane
Hex 13
Hex 14
Hex 1
Hex 10
Hex 11
Hex 6
Hex 15
Hex 9
Hex 2
Hex 7

FIG. 21A

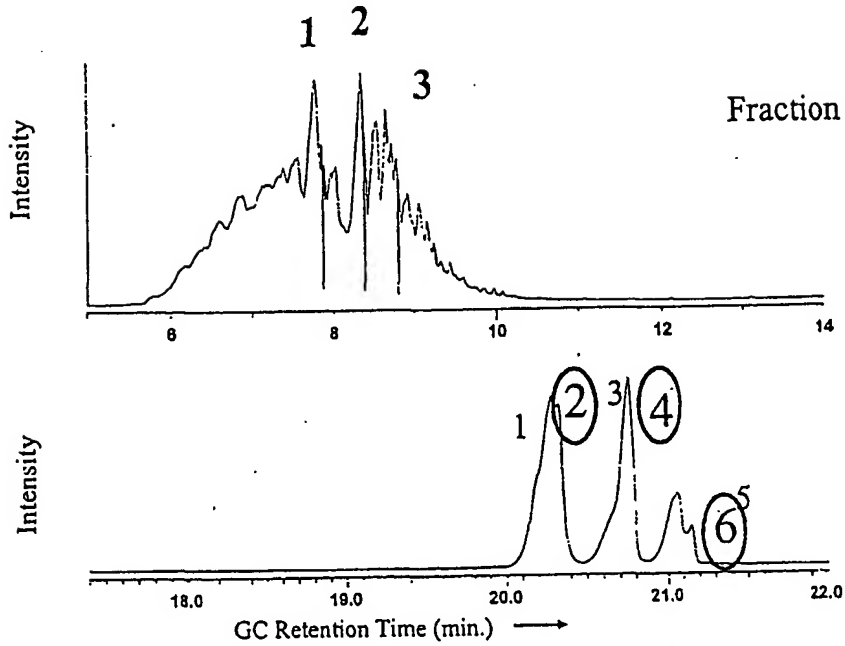


FIG. 21B

FIG. 22A

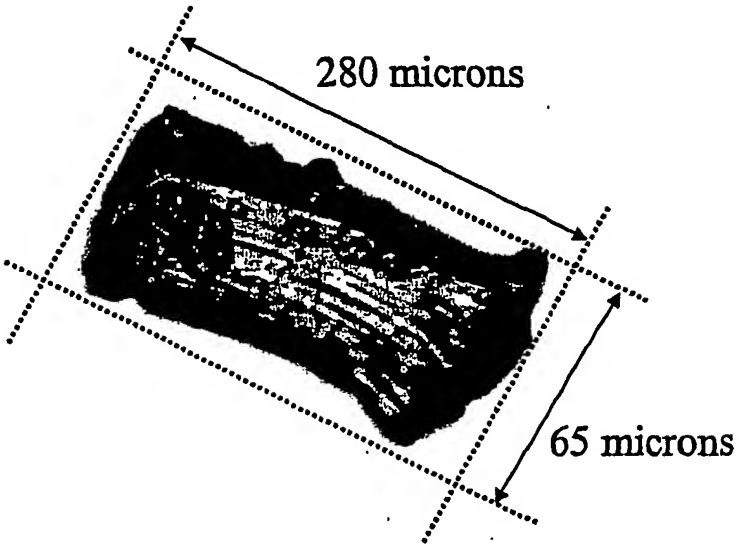


FIG. 22B

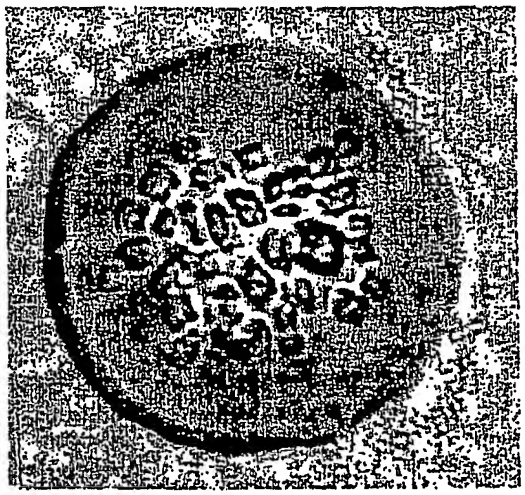


FIG. 22C

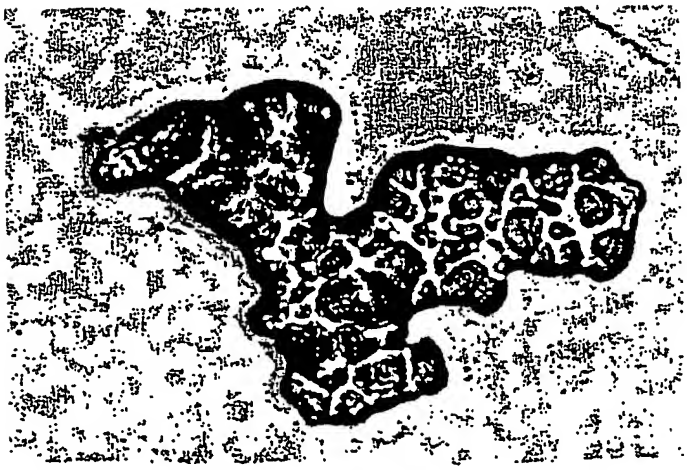


FIG. 23A

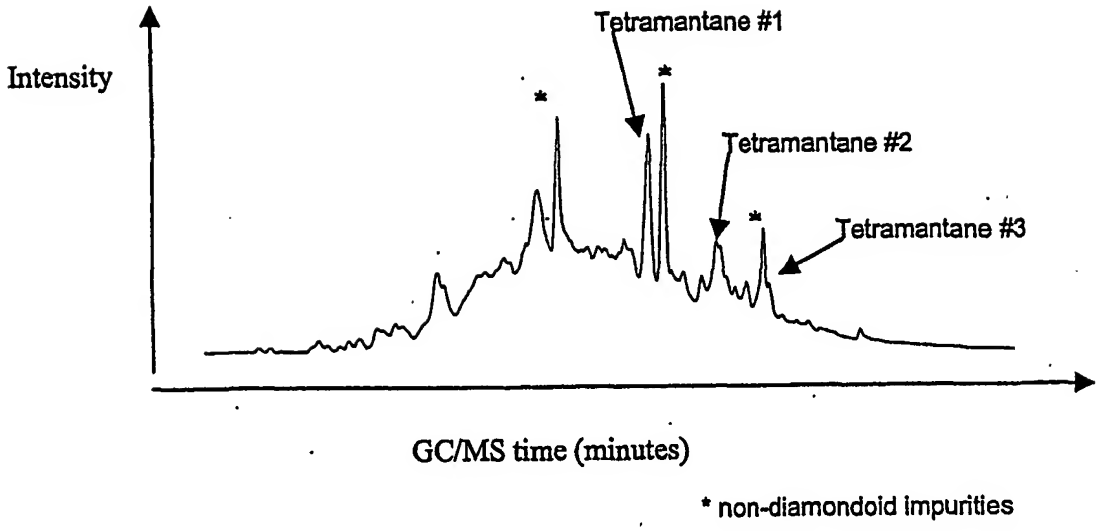


FIG. 23B

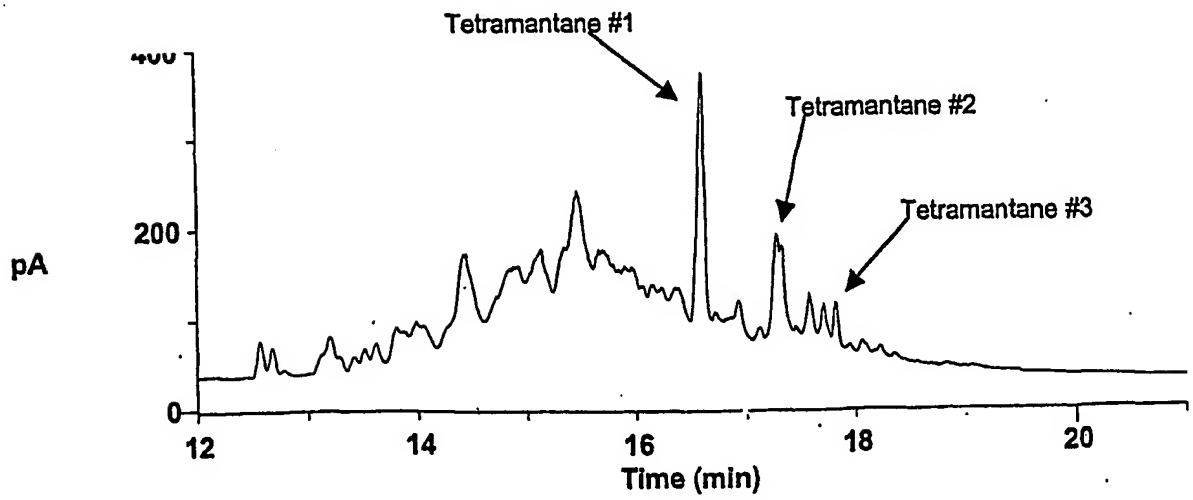


FIG. 24A

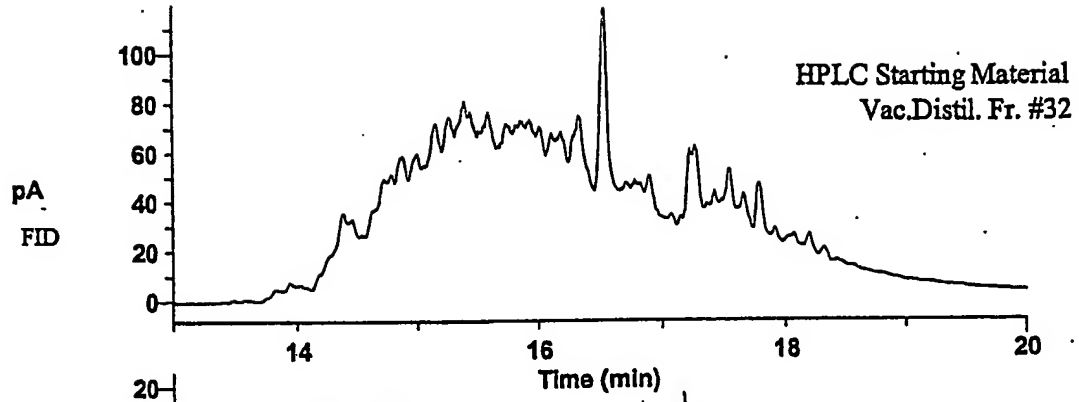


FIG. 24B

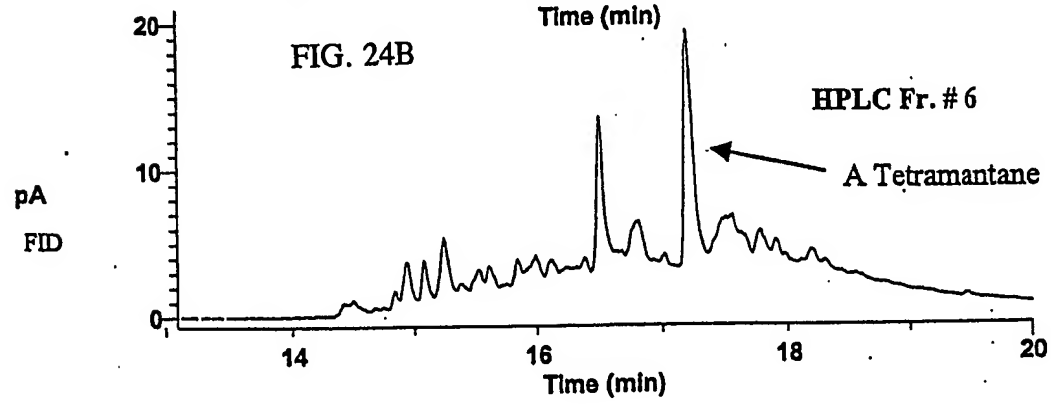


FIG. 25

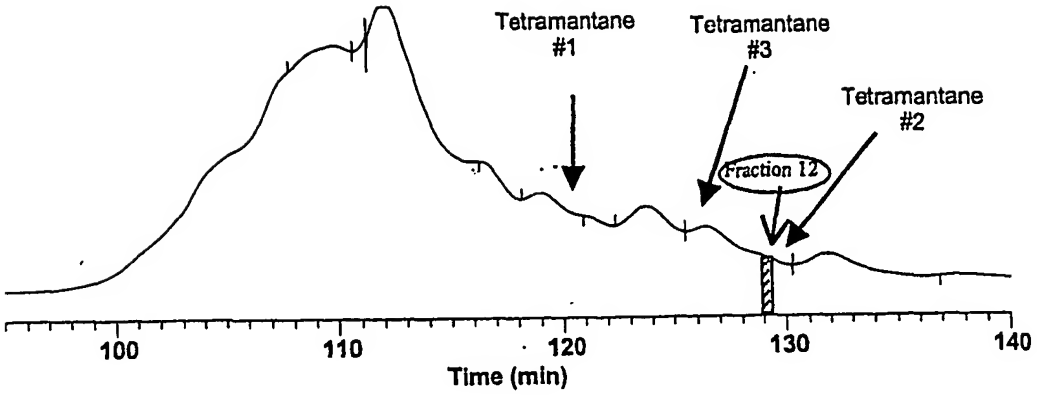

Tetramantane #1
Tetramantane #3
Tetramantane #2
Fraction 12
100
110
120
130
140
Time (min)

FIG. 26

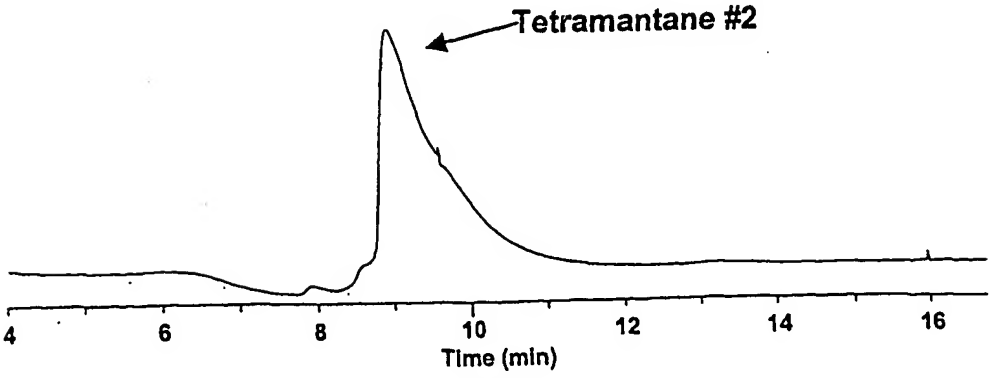

Tetramantane #2
4
6
8
10
12
14
16
Time (min)

FIG. 27A

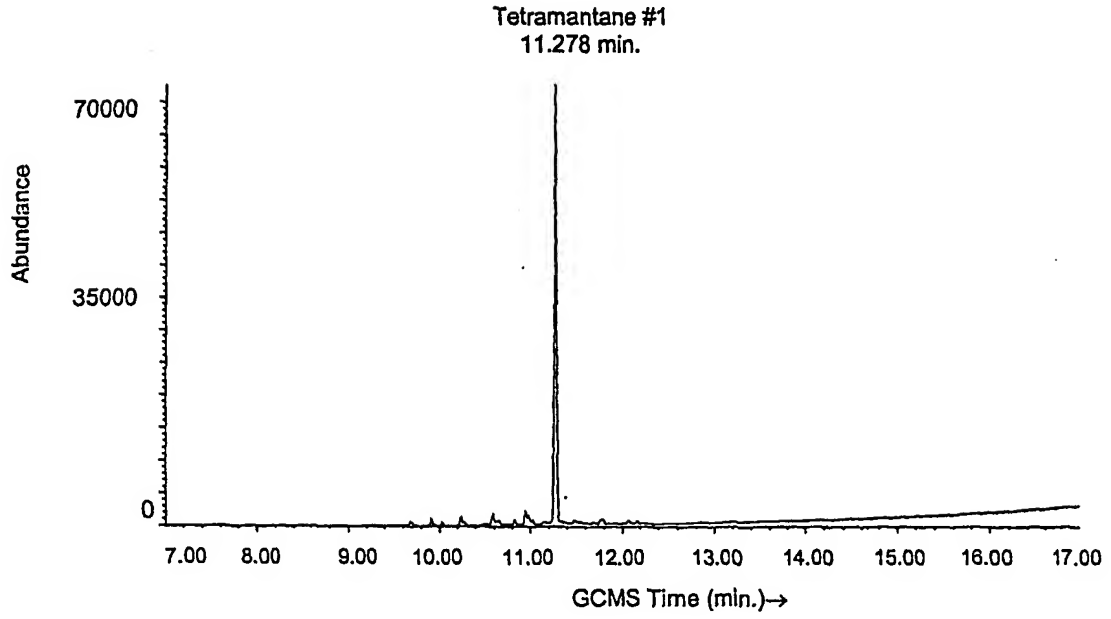


FIG. 27B

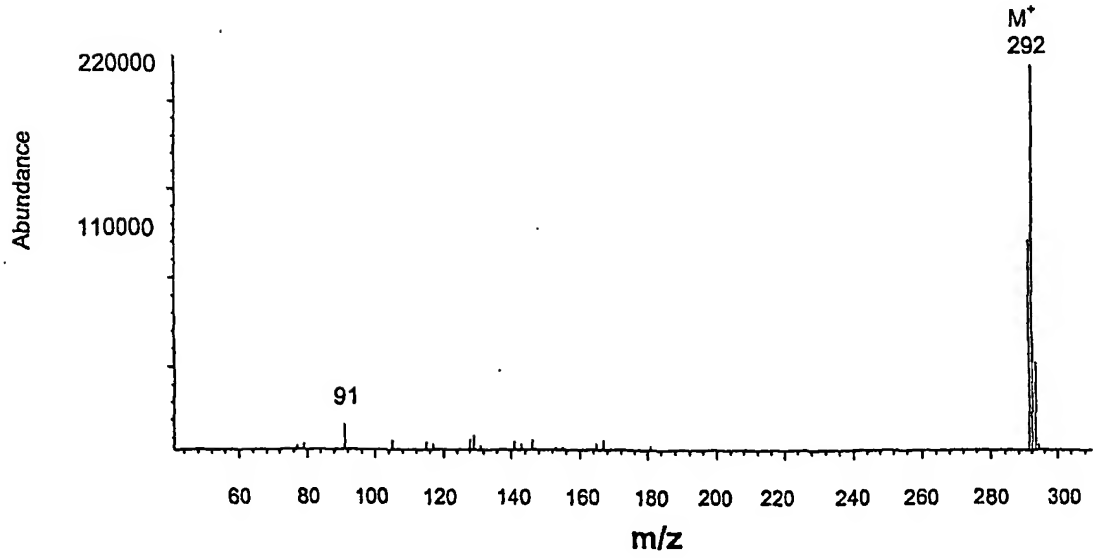


FIG. 28A

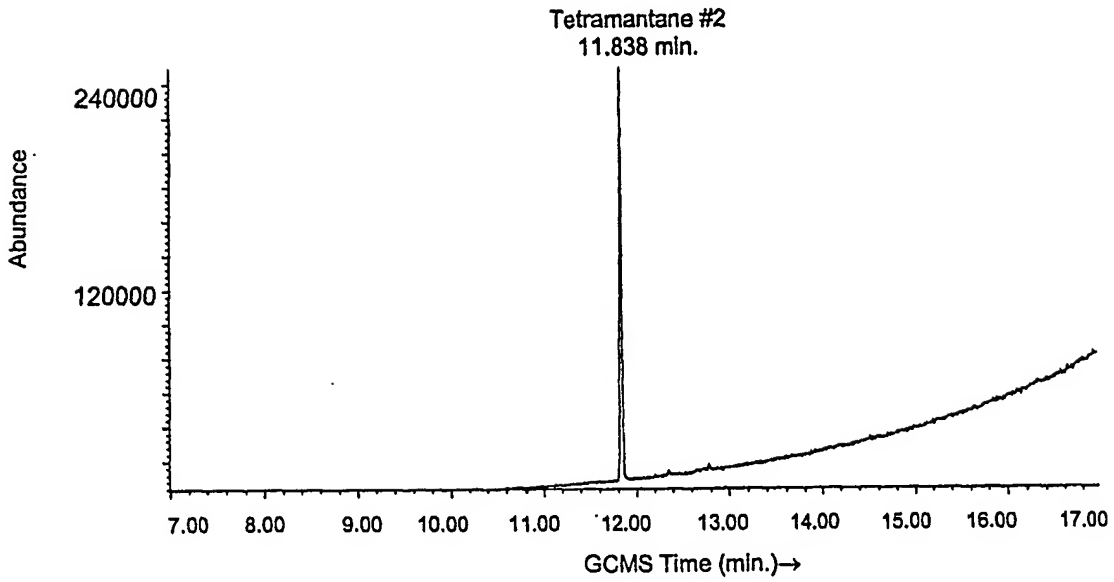


FIG. 28B

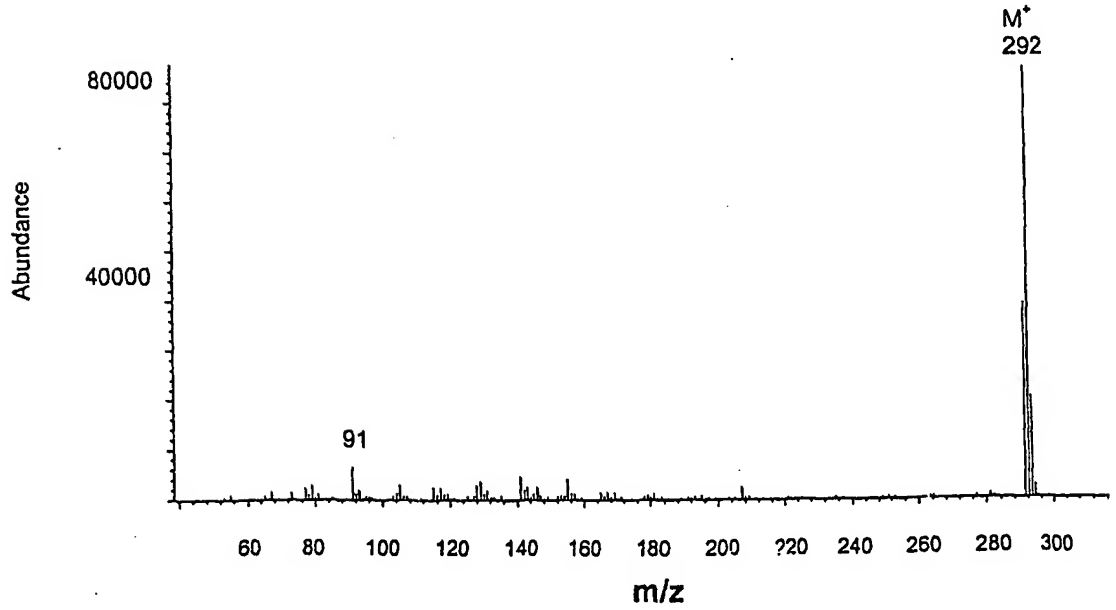


FIG. 29A

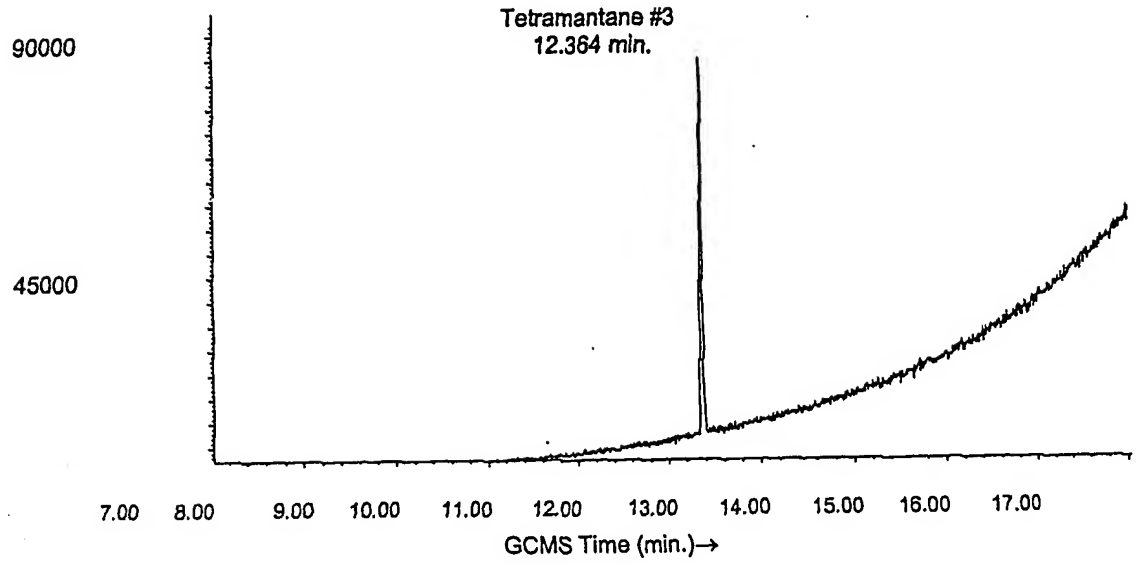


FIG. 29B

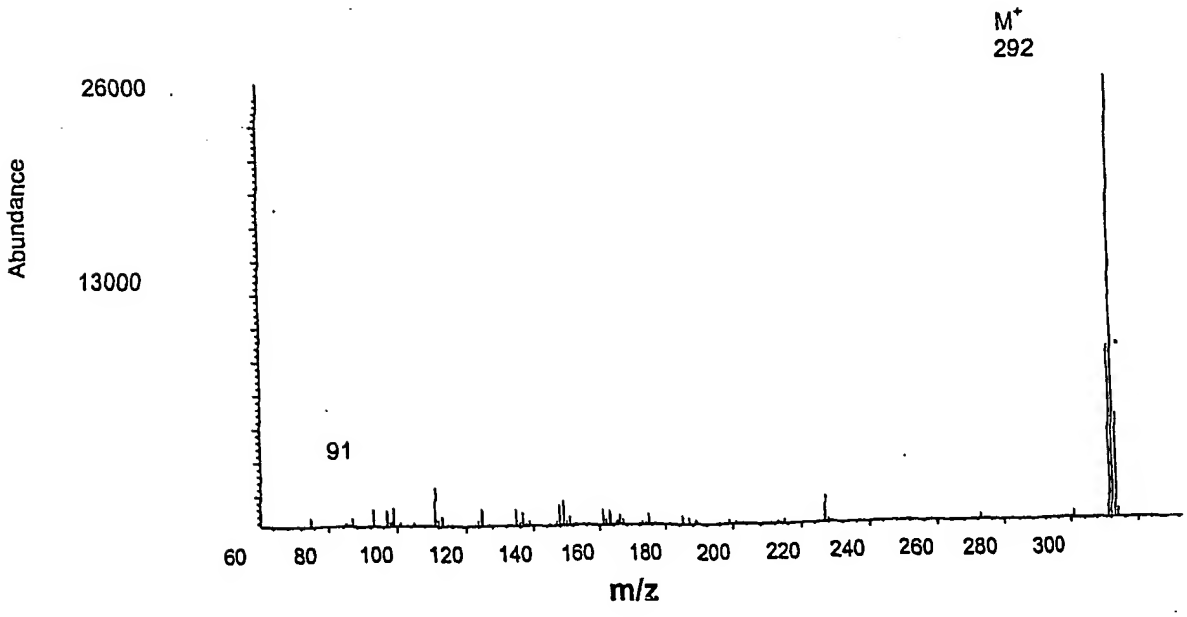


FIG. 30A

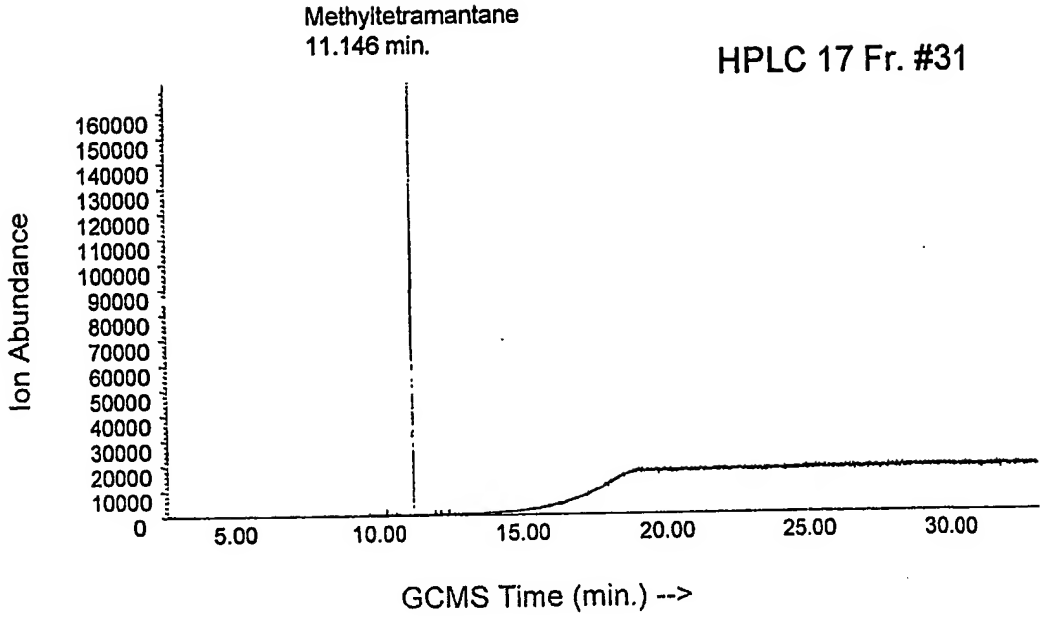


FIG. 30B

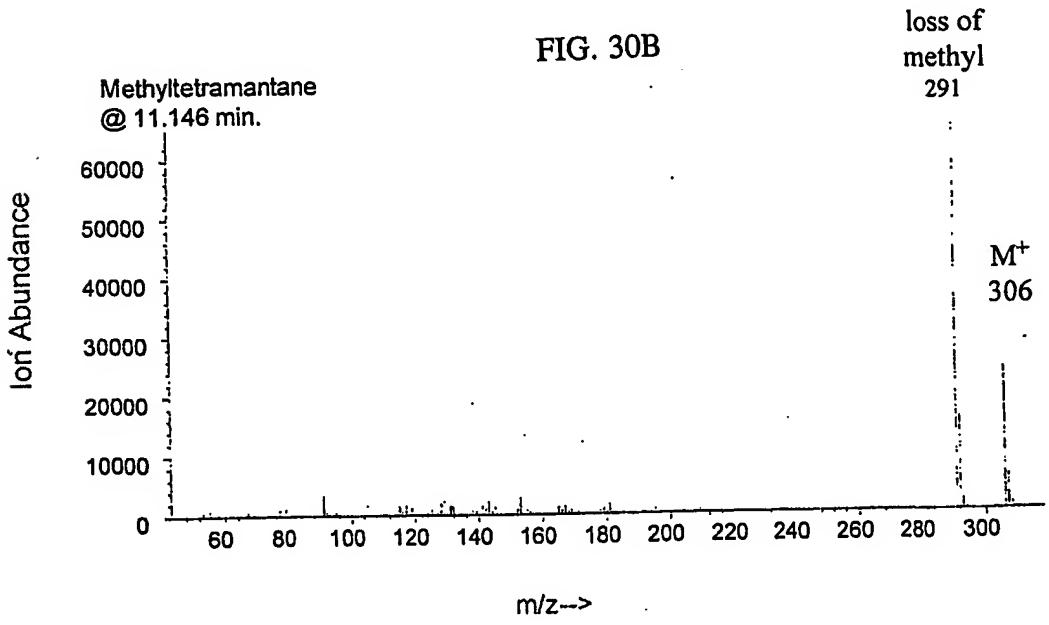


FIG. 31

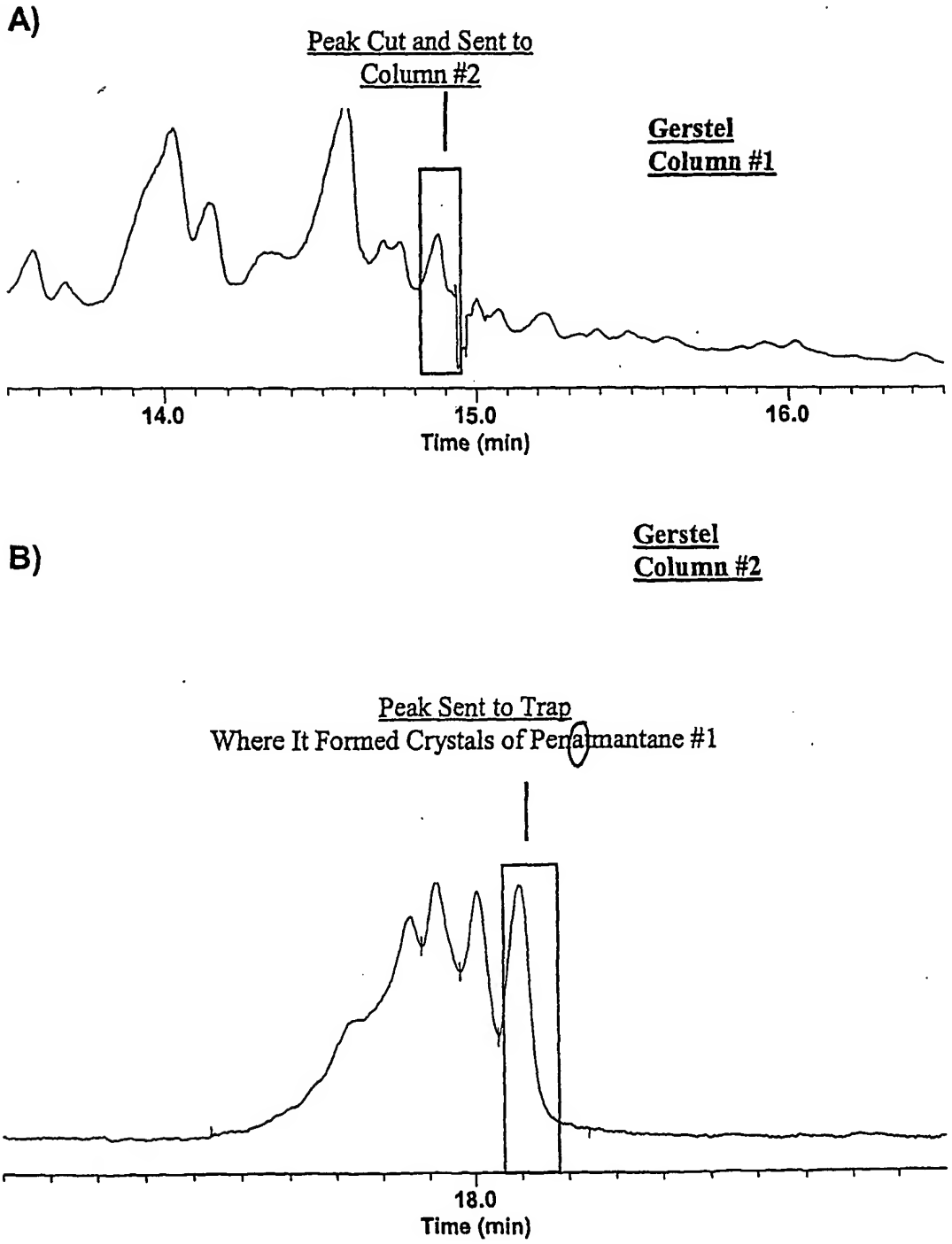
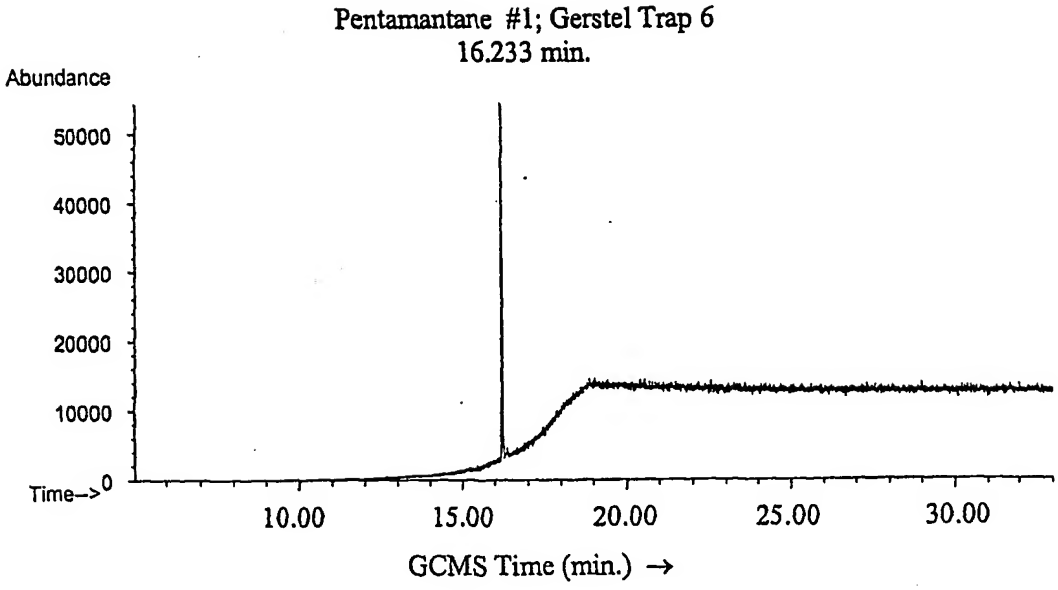

A)
Peak Cut and Sent to
Column #2
Gerstel
Column #1
14.0
15.0
16.0
Time (min)
B)
Gerstel
Column #2
Peak Sent to Trap
Where It Formed Crystals of Pentamantane #1
18.0
Time (min)

FIG. 32

A.


Pentamantane #1; Gerstel Trap 6
16.233 min.
Abundance
50000
40000
30000
20000
10000
Time-->0
10.00
15.00
20.00
25.00
30.00
GCMS Time (min.) →

B.

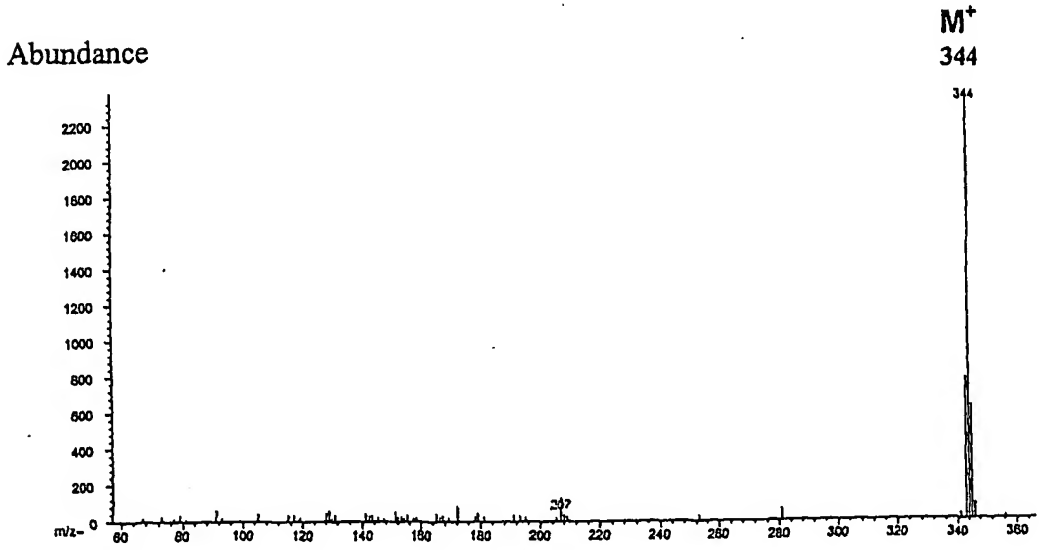
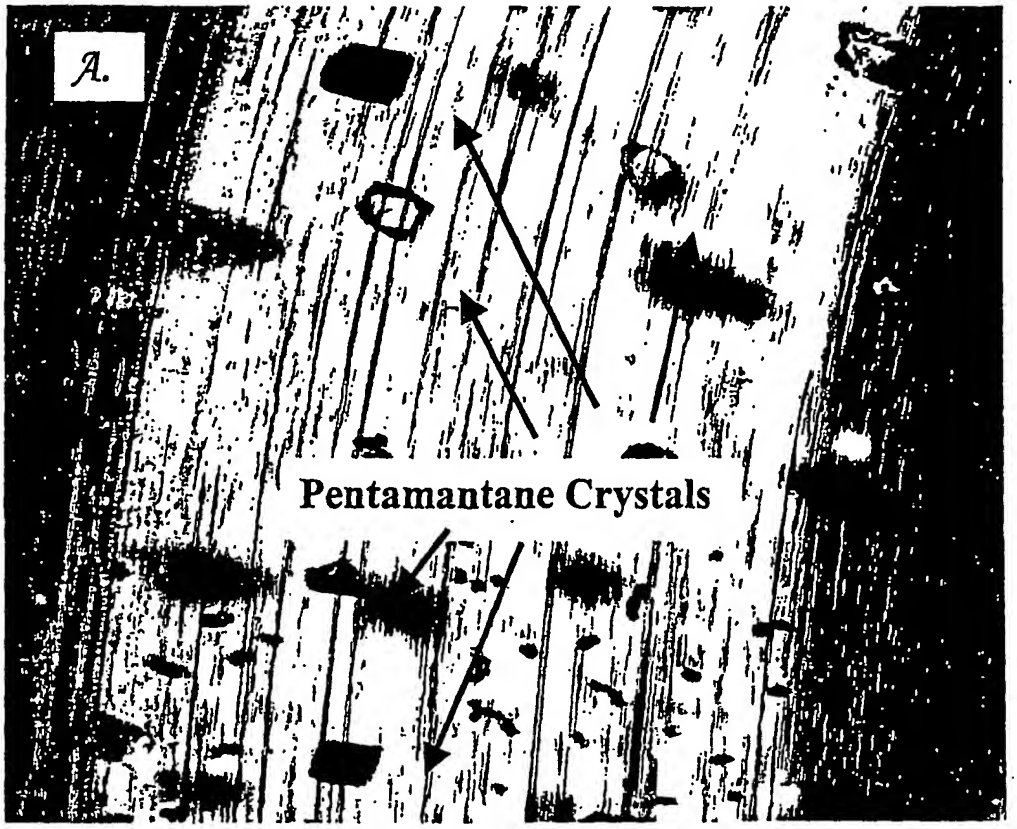

Abundance
M+
344
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
m/z-
0
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360

FIG. 33



B.

Isolated and Crystallized Pentamantanes
(2 of 10 possible)

(Crystal is approximately 250 microns in diameter)

FIG. 34

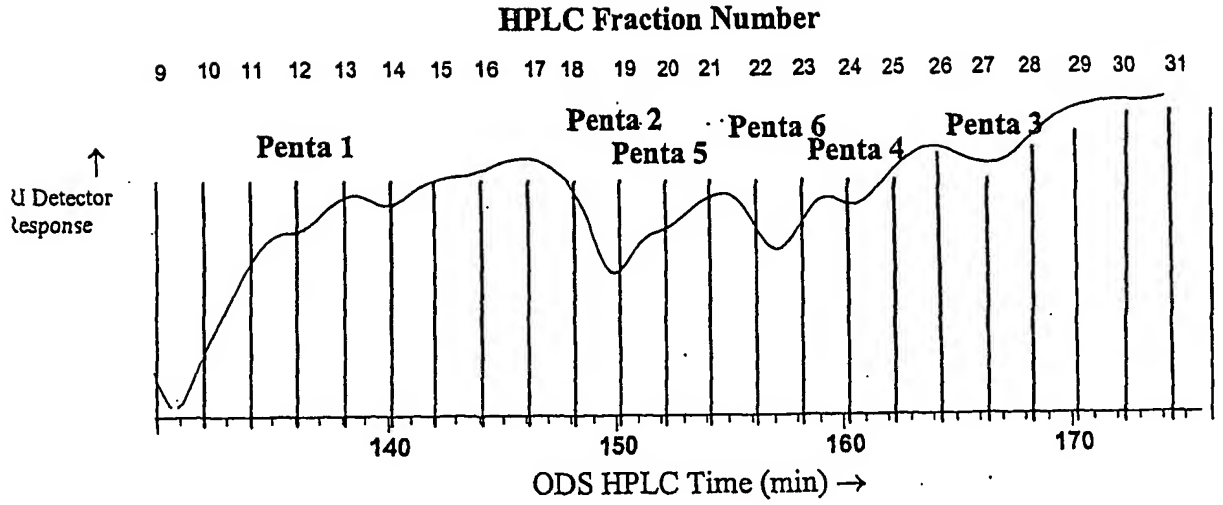

HPLC Fraction Number
9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31
Penta 1
Penta 2
Penta 5
Penta 6
Penta 4
Penta 3
U Detector
Response
140
150
160
170
ODS HPLC Time (min) →

FIG. 35

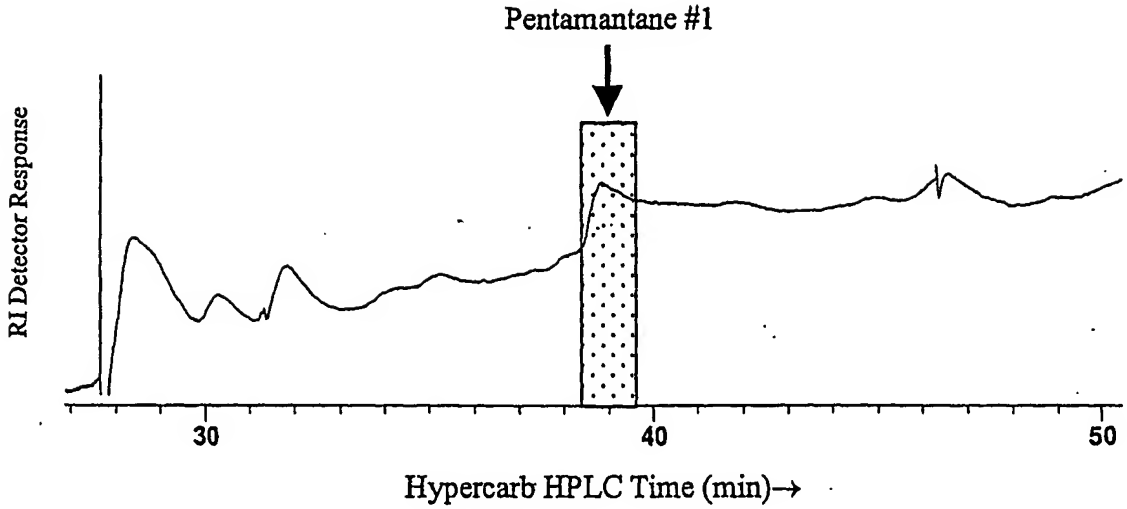

Pentamantane #1
RI Detector Response
30
40
50
Hypercarb HPLC Time (min)→

FIG. 36A

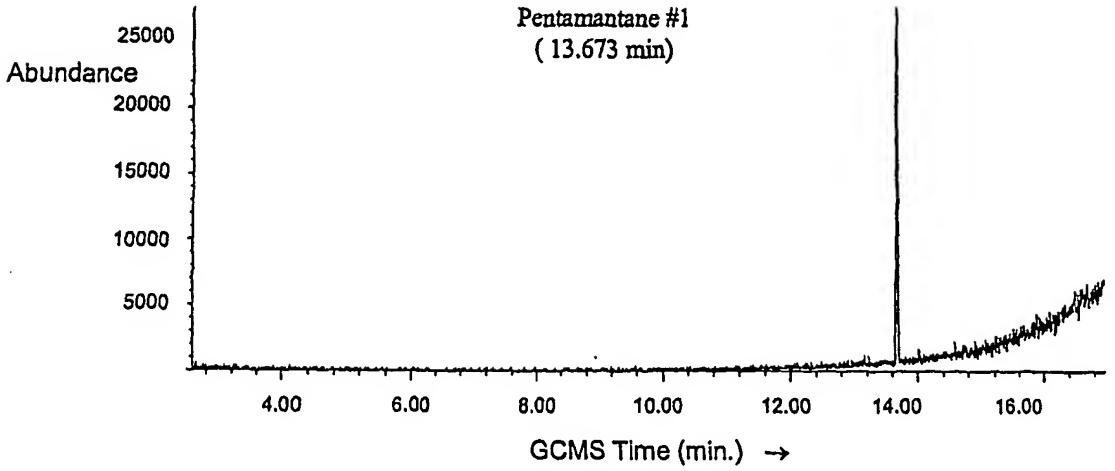


FIG. 36B

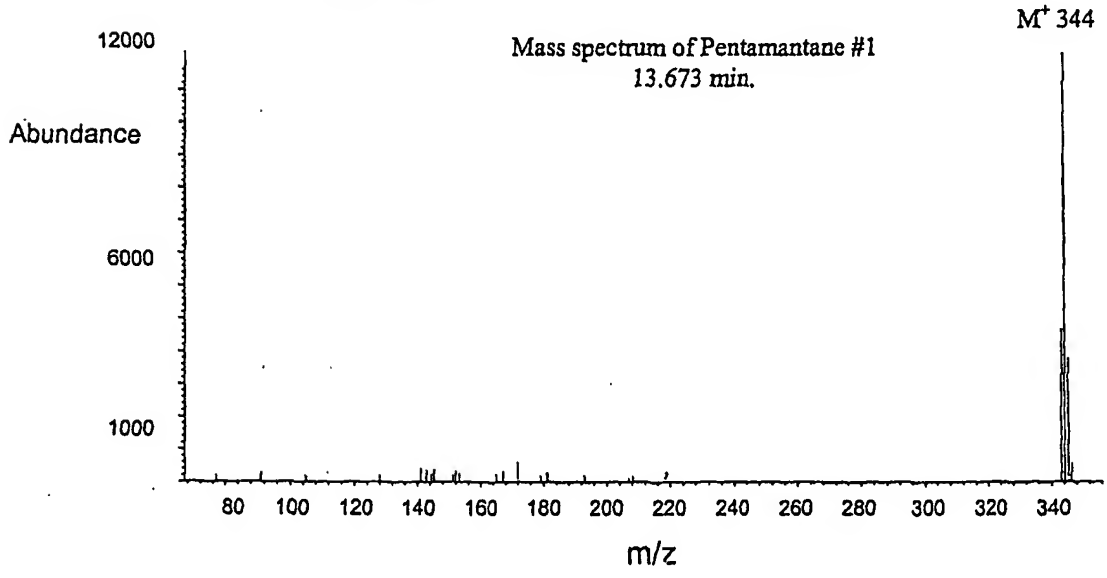
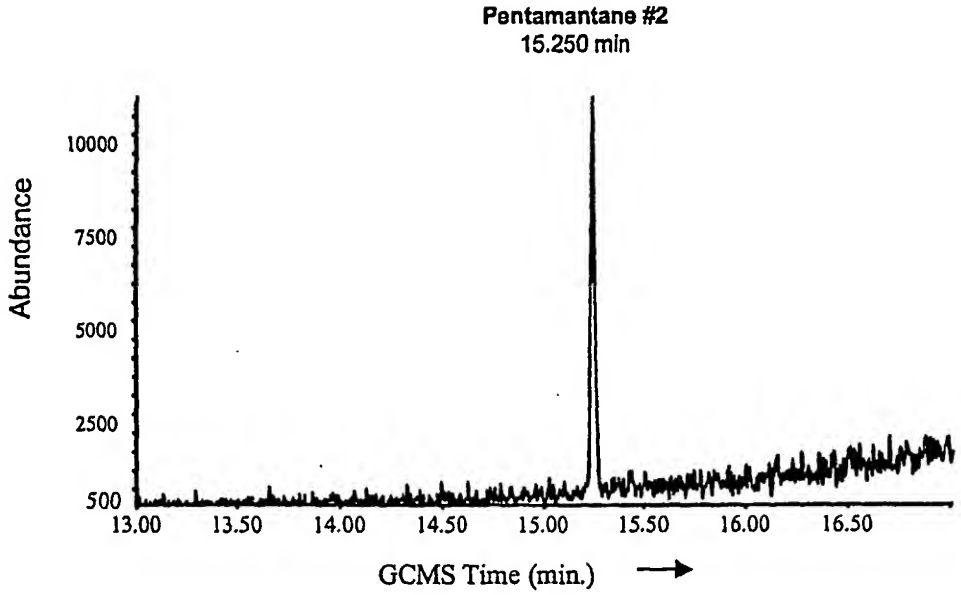


FIG. 37

A.


Pentamantane #2
15.250 min
Abundance
10000
7500
5000
2500
500
13.00
13.50
14.00
14.50
15.00
15.50
16.00
16.50
GCMS Time (min.)

B.

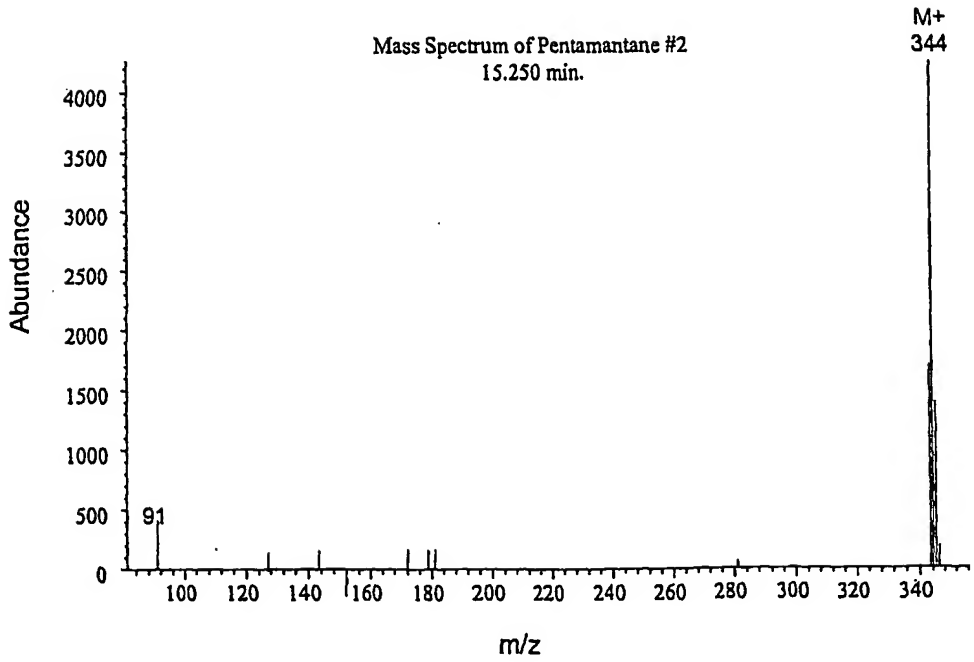
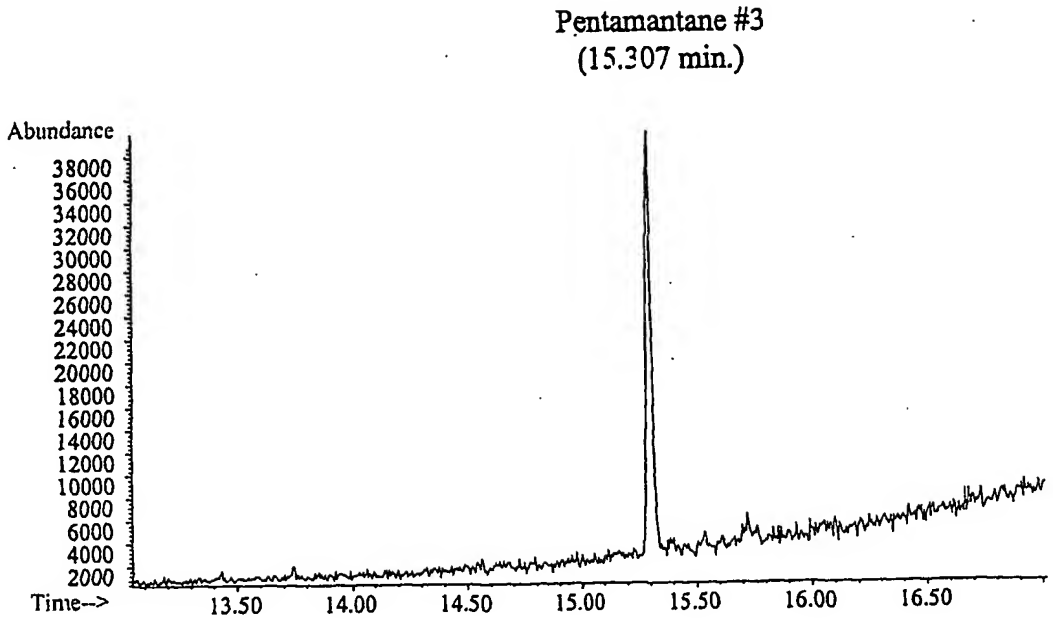

Mass Spectrum of Pentamantane #2
15.250 min.
M+
344
91
Abundance
4000
3500
3000
2500
2000
1500
1000
500
0
100
120
140
160
180
200
220
240
260
280
300
320
340
m/z

FIG. 38

A.


Pentamantane #3
(15.307 min.)
Abundance
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
Time-->
13.50
14.00
14.50
15.00
15.50
16.00
16.50

B.

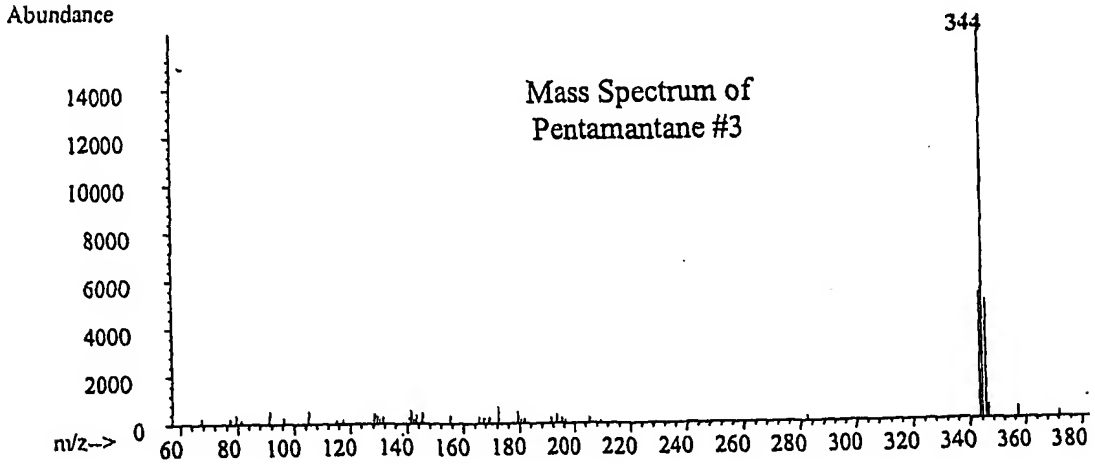
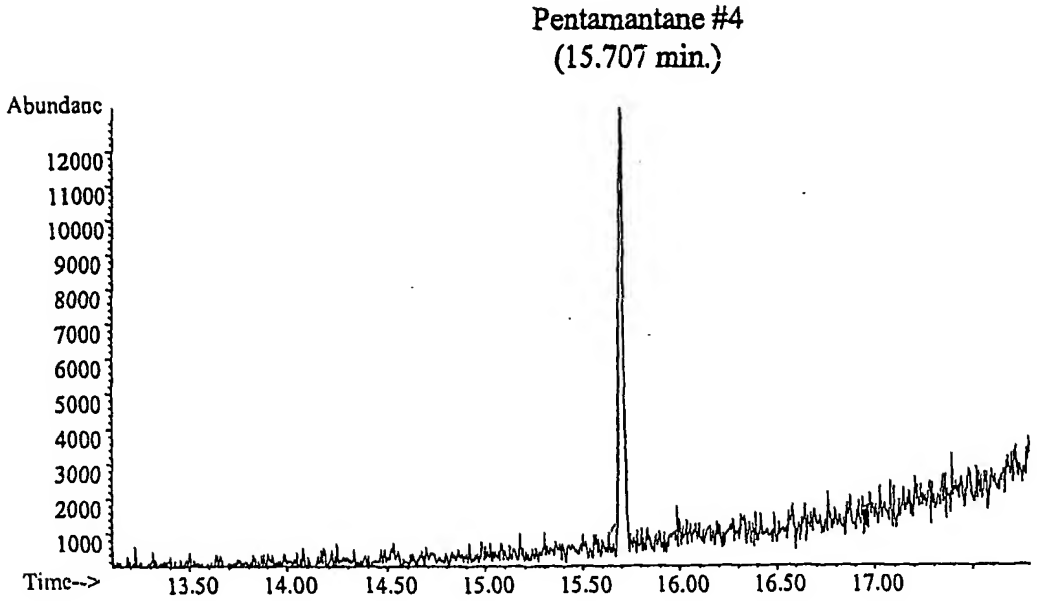

Abundance
344
Mass Spectrum of
Pentamantane #3
14000
12000
10000
8000
6000
4000
2000
0
m/z-->
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380

FIG. 39

A.


Pentamantane #4
(15.707 min.)
Abundanc
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
Time-->
13.50
14.00
14.50
15.00
15.50
16.00
16.50
17.00

B,

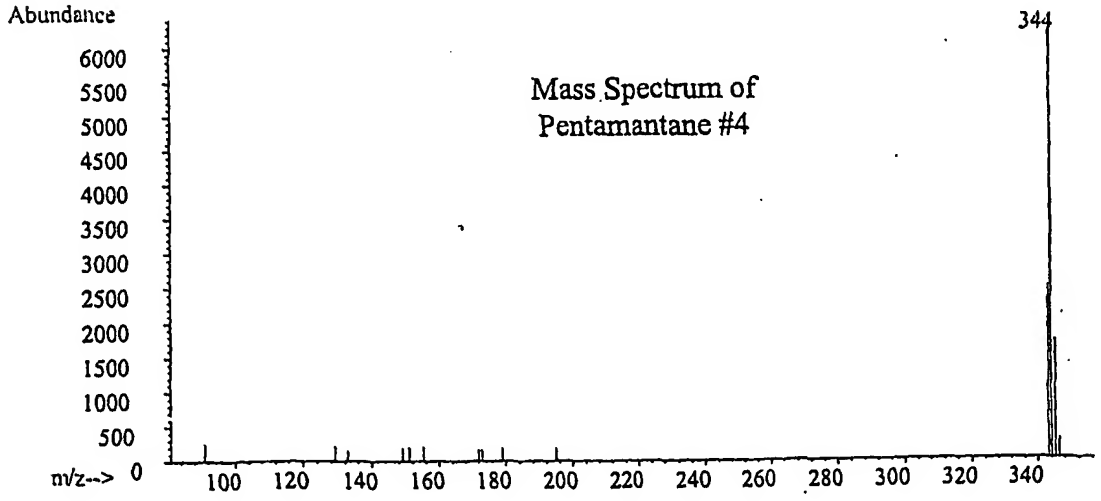
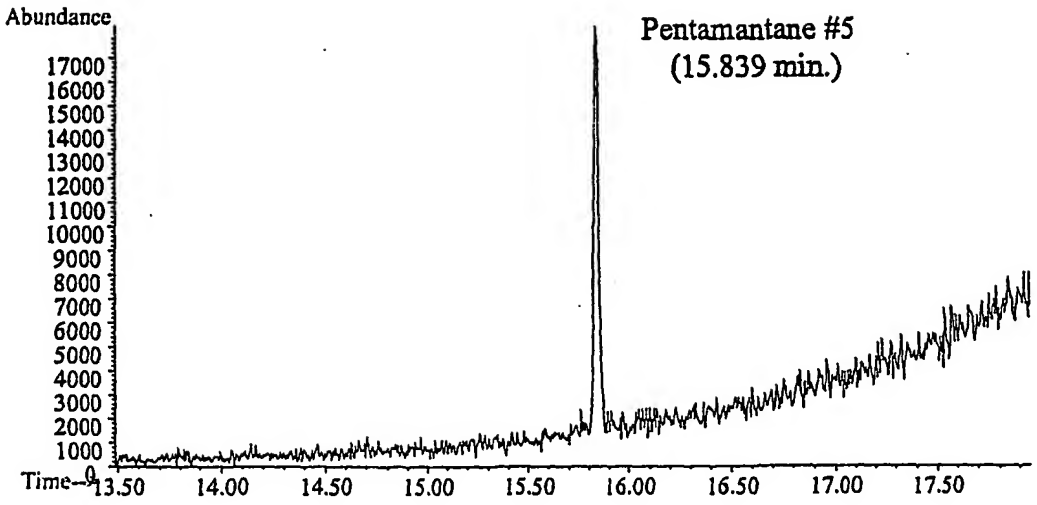

Abundance
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
m/z--> 0
Mass Spectrum of
Pentamantane #4
344
100
120
140
160
180
200
220
240
260
280
300
320
340

FIG. 40

A.


Abundance
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
Time--> 0
13.50
14.00
14.50
15.00
15.50
16.00
16.50
17.00
17.50
Pentamantane #5
(15.839 min.)

B.

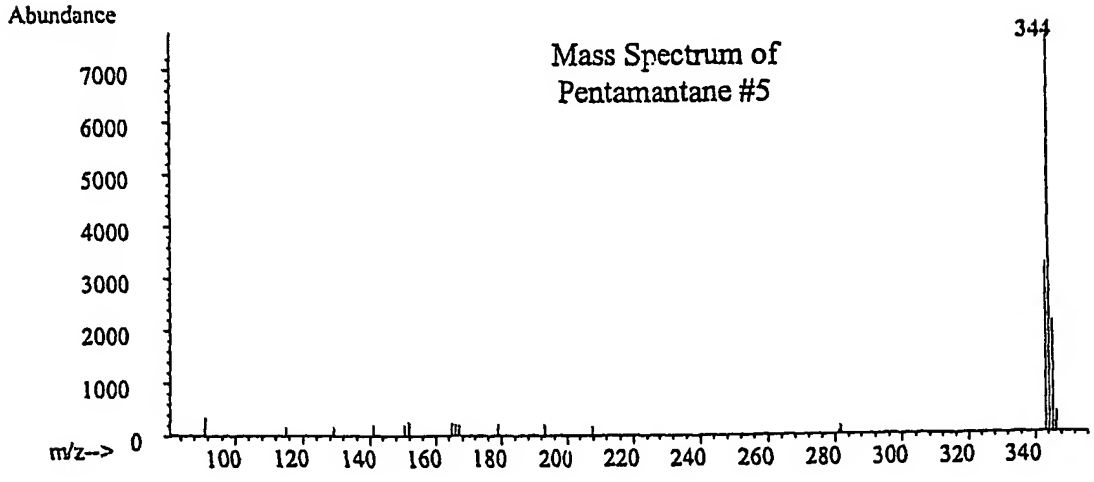
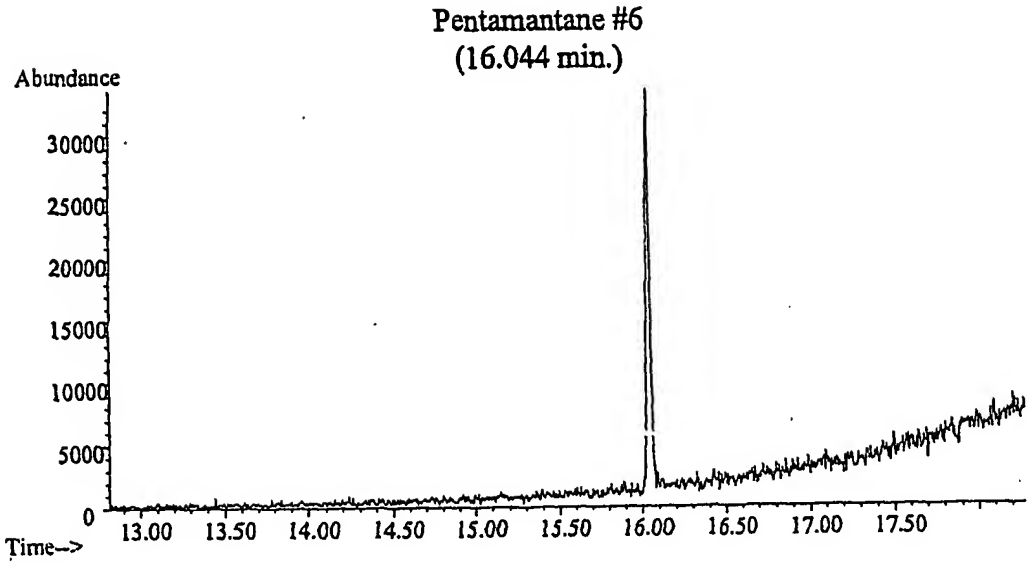

Abundance
7000
6000
5000
4000
3000
2000
1000
m/z--> 0
100
120
140
160
180
200
220
240
260
280
300
320
340
344
Mass Spectrum of
Pentamantane #5

FIG. 41

A.


Pentamantane #6
(16.044 min.)
Abundance
30000
25000
20000
15000
10000
5000
0
Time-->
13.00
13.50
14.00
14.50
15.00
15.50
16.00
16.50
17.00
17.50

B.

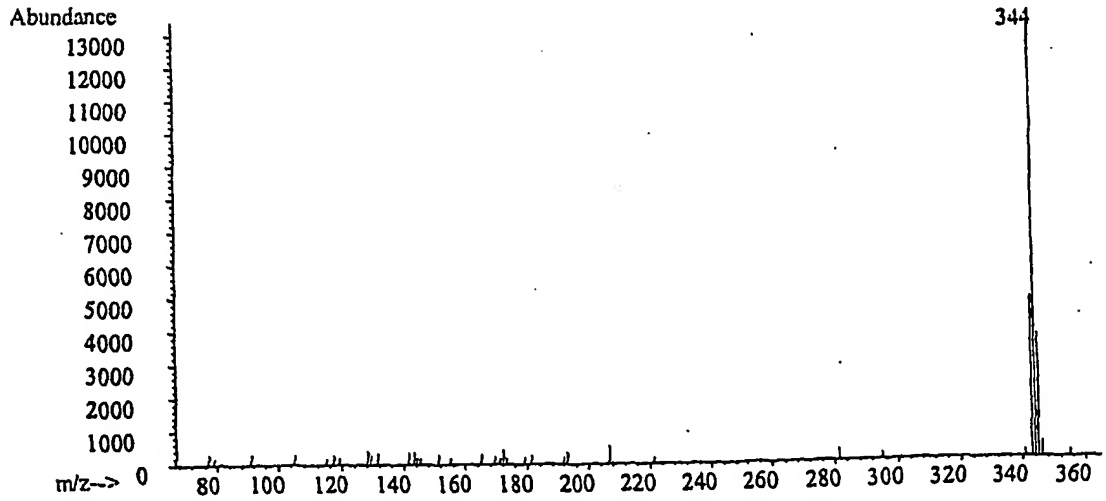
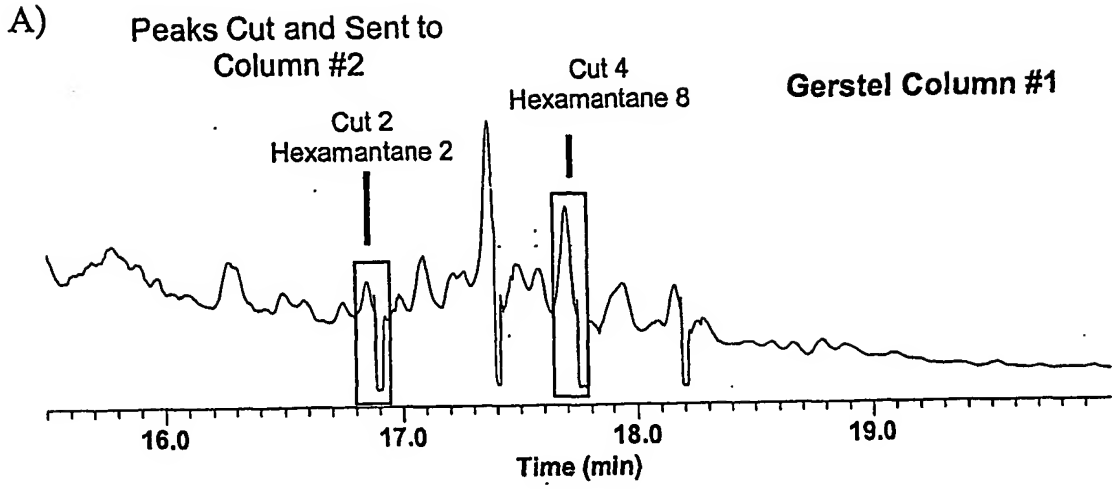

Mass Spectrum of
Pentamantane #6
Abundance
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
m/z-->
0
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
344

FIG. 42


A)
Peaks Cut and Sent to Column #2
Cut 2 Hexamantane 2
Cut 4 Hexamantane 8
Gerstel Column #1
16.0
17.0
18.0
19.0
Time (min)

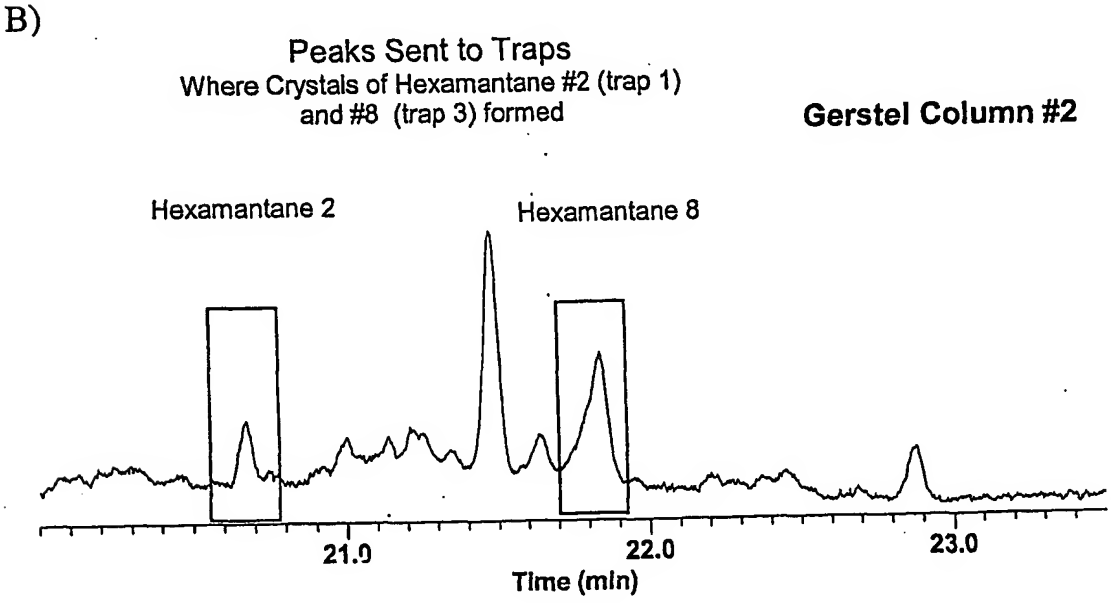
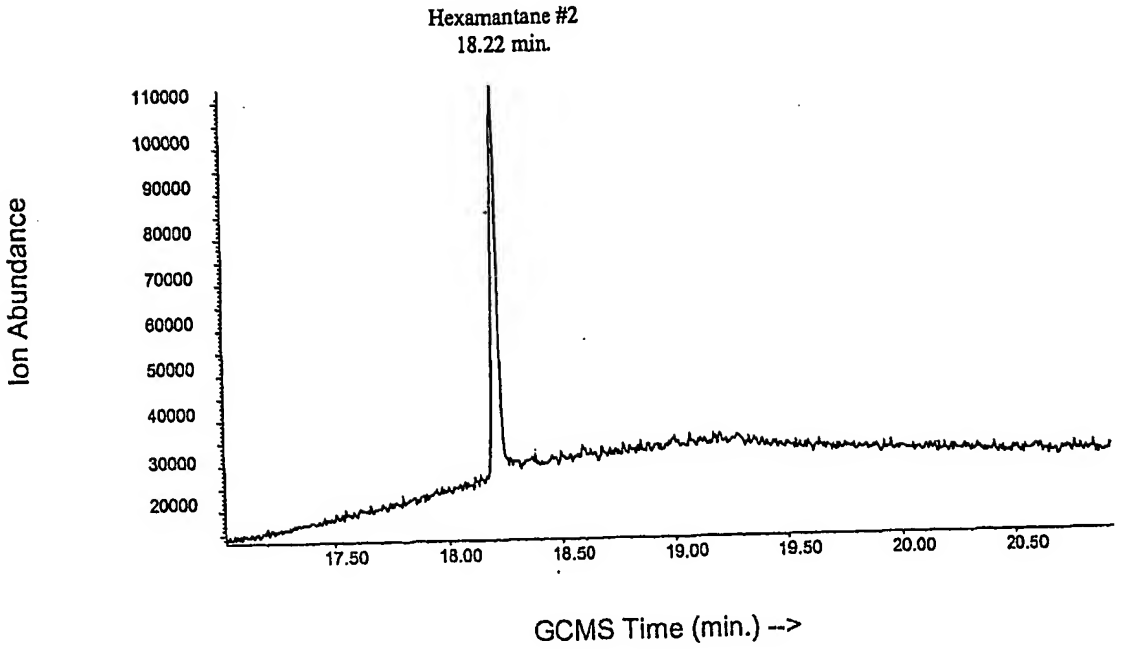

B)
Peaks Sent to Traps
Where Crystals of Hexamantane #2 (trap 1) and #8 (trap 3) formed
Gerstel Column #2
Hexamantane 2
Hexamantane 8
21.0
22.0
23.0
Time (min)

FIG. 43

A)


Hexamantane #2
18.22 min.
Ion Abundance
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
17.50
18.00
18.50
19.00
19.50
20.00
20.50
GCMS Time (min.) -->

B)

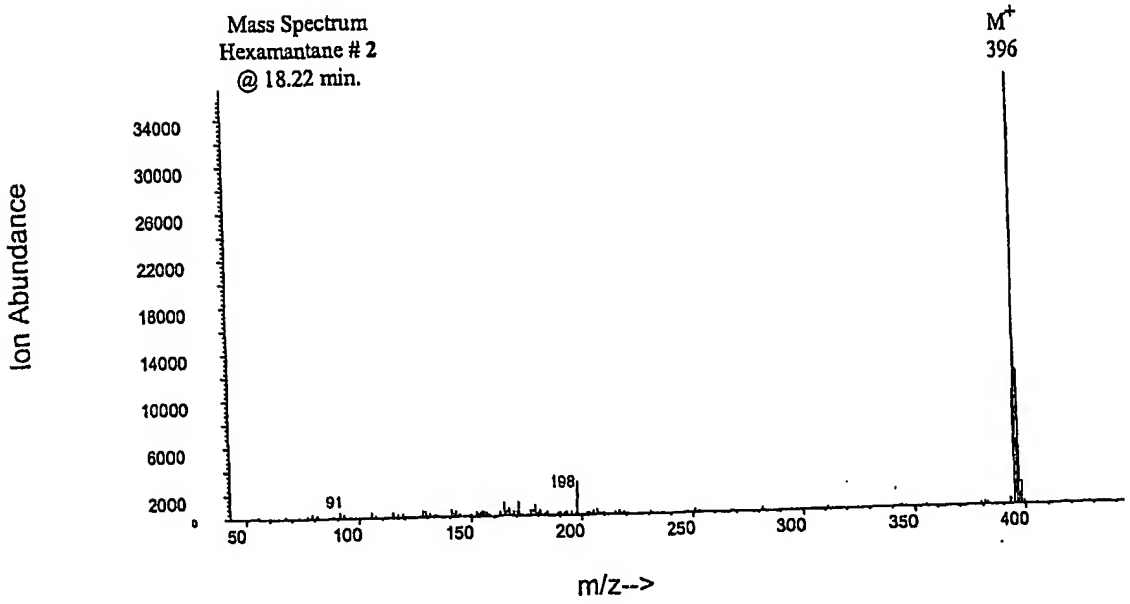
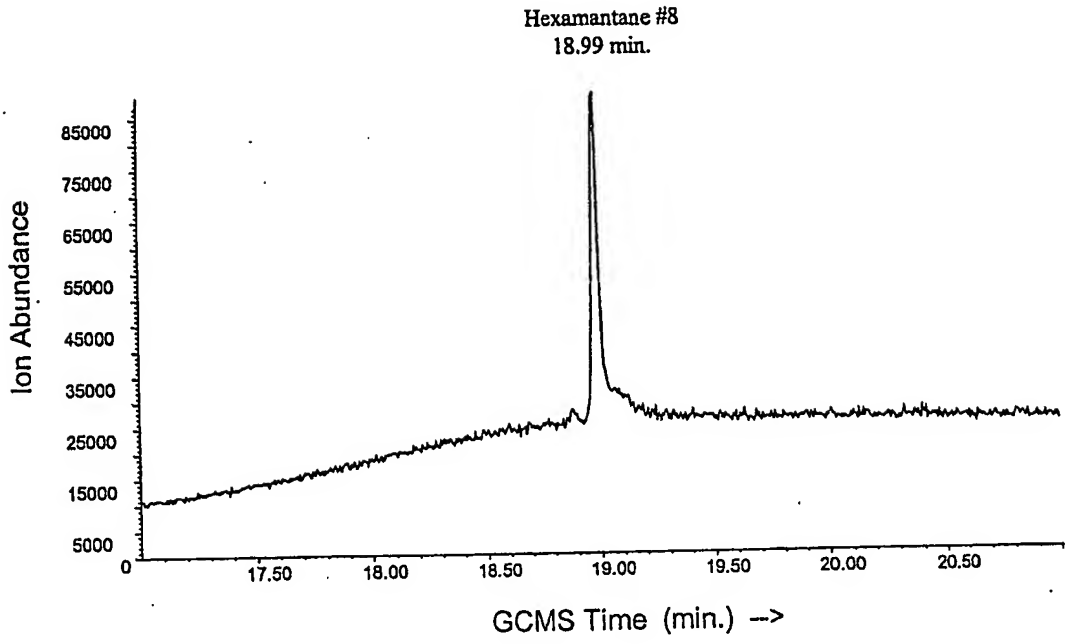

Mass Spectrum
Hexamantane # 2
@ 18.22 min.
M+
396
Ion Abundance
34000
30000
26000
22000
18000
14000
10000
6000
2000
91
198
50
100
150
200
250
300
350
400
m/z-->

FIG. 44

A)


Hexamantane #8
18.99 min.
Ion Abundance
85000
75000
65000
55000
45000
35000
25000
15000
5000
0
17.50
18.00
18.50
19.00
19.50
20.00
20.50
GCMS Time (min.) -->

B)

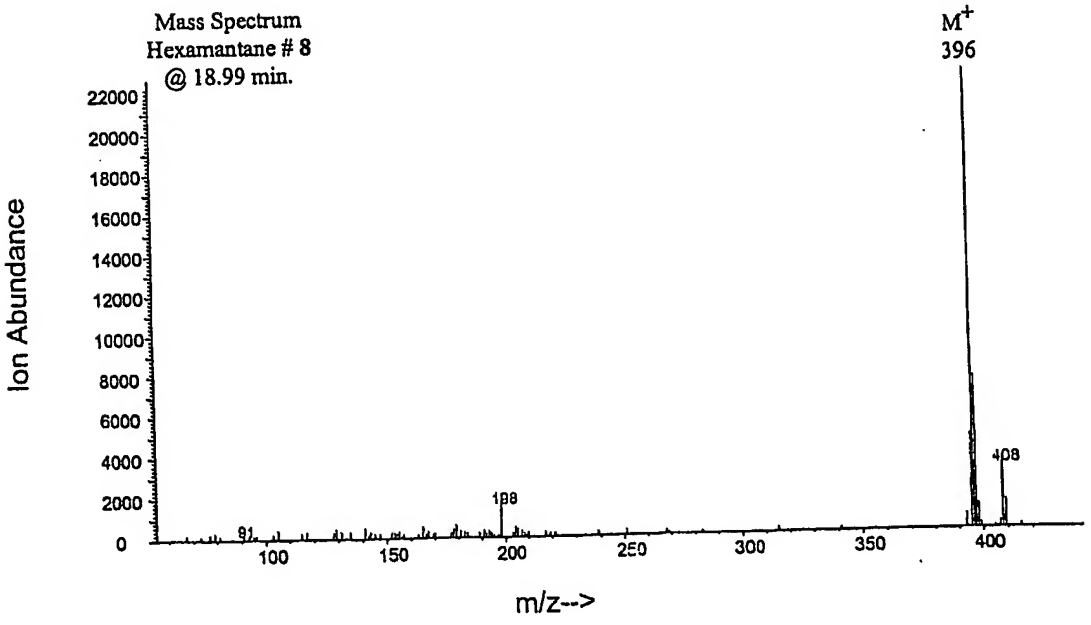
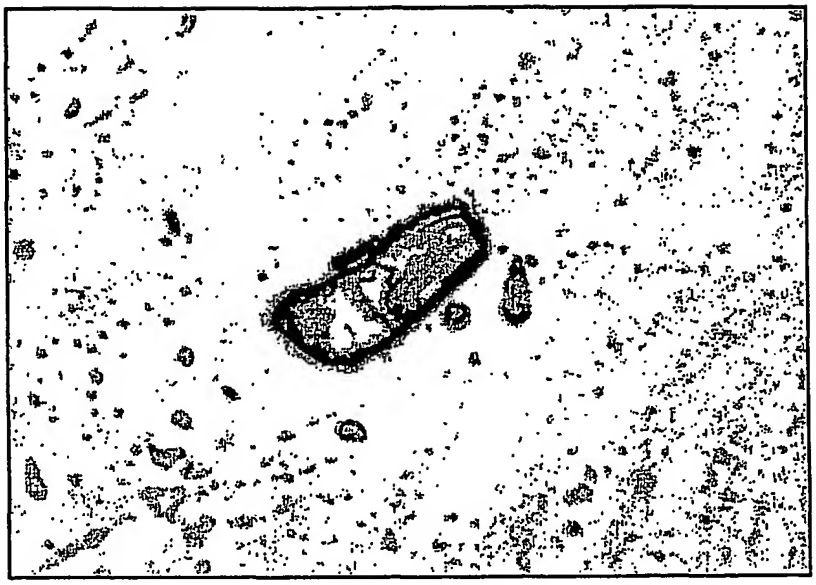

Mass Spectrum
Hexamantane # 8
@ 18.99 min.
M+
396
Ion Abundance
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
91
198
408
100
150
200
250
300
350
400
m/z-->

FIG. 45

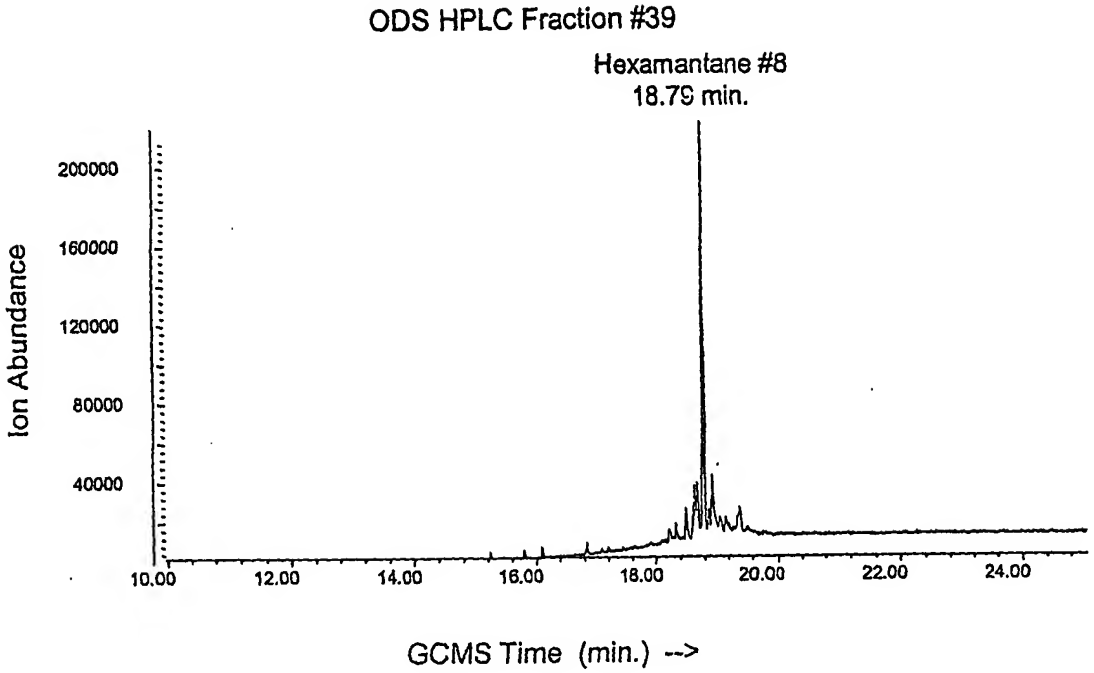


Hexamantane #2 Crystals

FIG. 46

FIG. 47

A)


ODS HPLC Fraction #39
Hexamantane #8
18.79 min.
Ion Abundance
200000
160000
120000
80000
40000
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
GCMS Time (min.) -->

B)

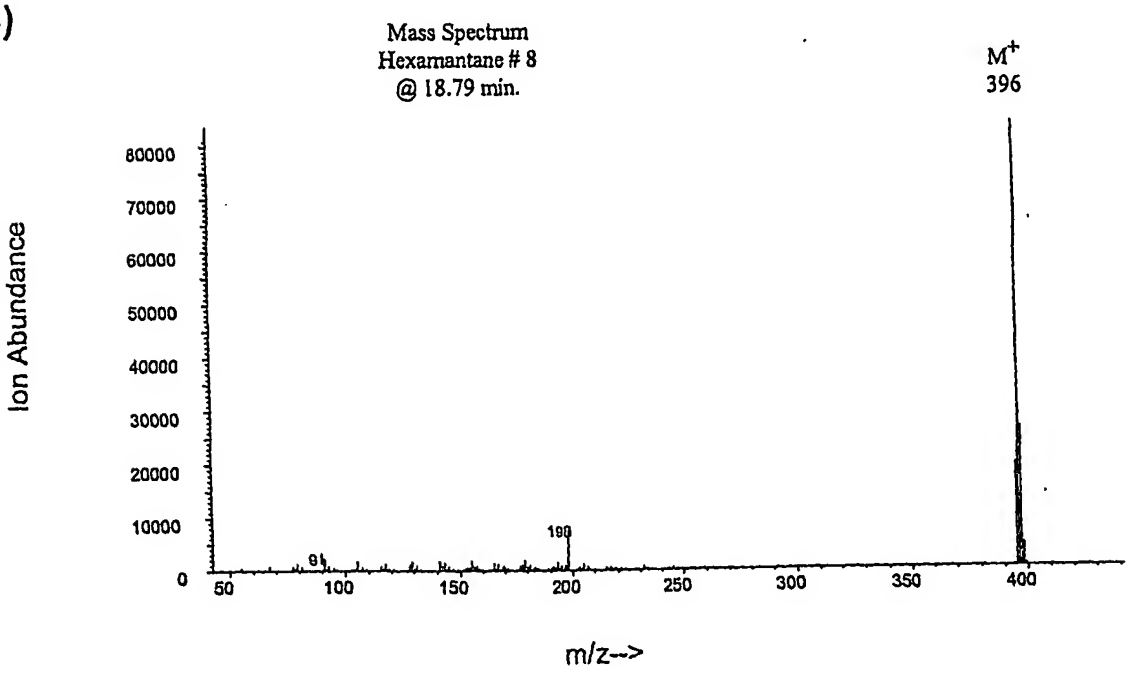
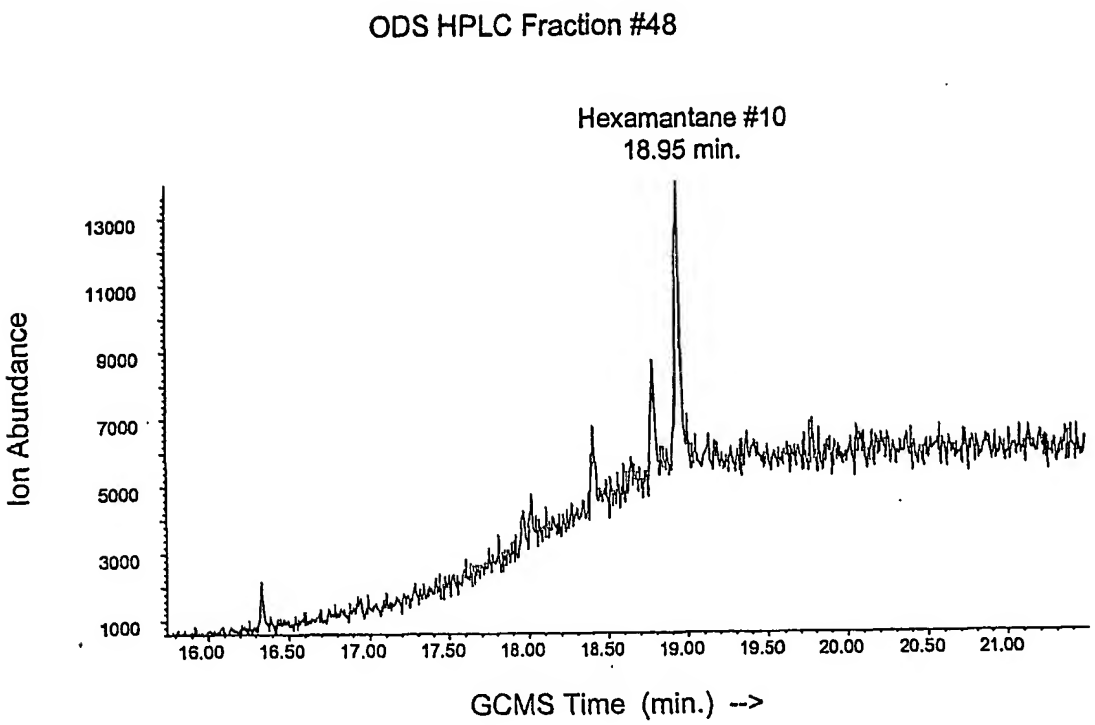

Mass Spectrum
Hexamantane # 8
@ 18.79 min.
M+
396
Ion Abundance
80000
70000
60000
50000
40000
30000
20000
10000
0
91
190
50
100
150
200
250
300
350
400
m/z-->

FIG. 48

A)


ODS HPLC Fraction #48
Hexamantane #10
18.95 min.
Ion Abundance
13000
11000
9000
7000
5000
3000
1000
16.00
16.50
17.00
17.50
18.00
18.50
19.00
19.50
20.00
20.50
21.00
GCMS Time (min.) -->

B)

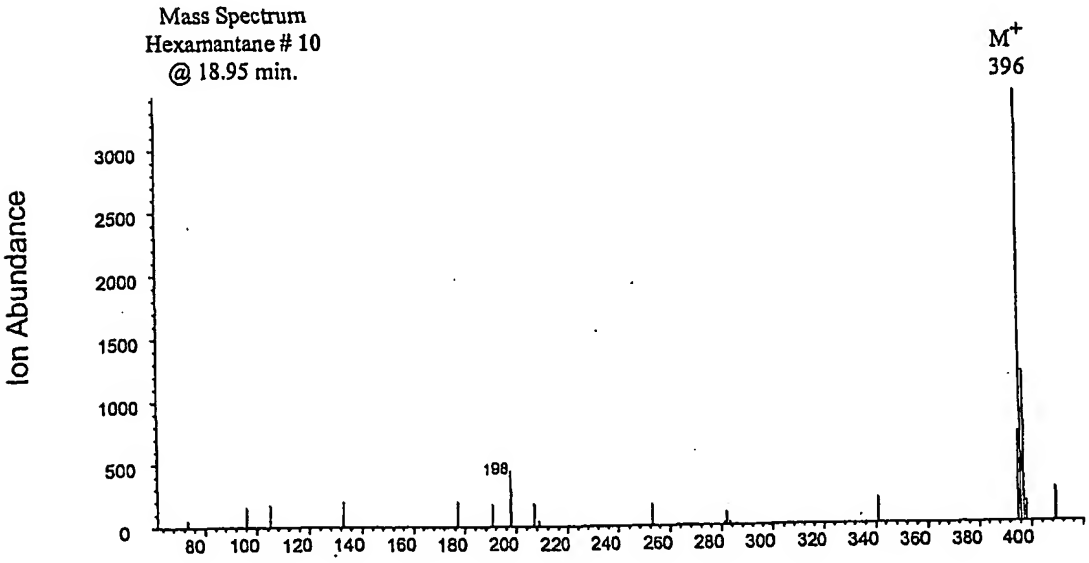
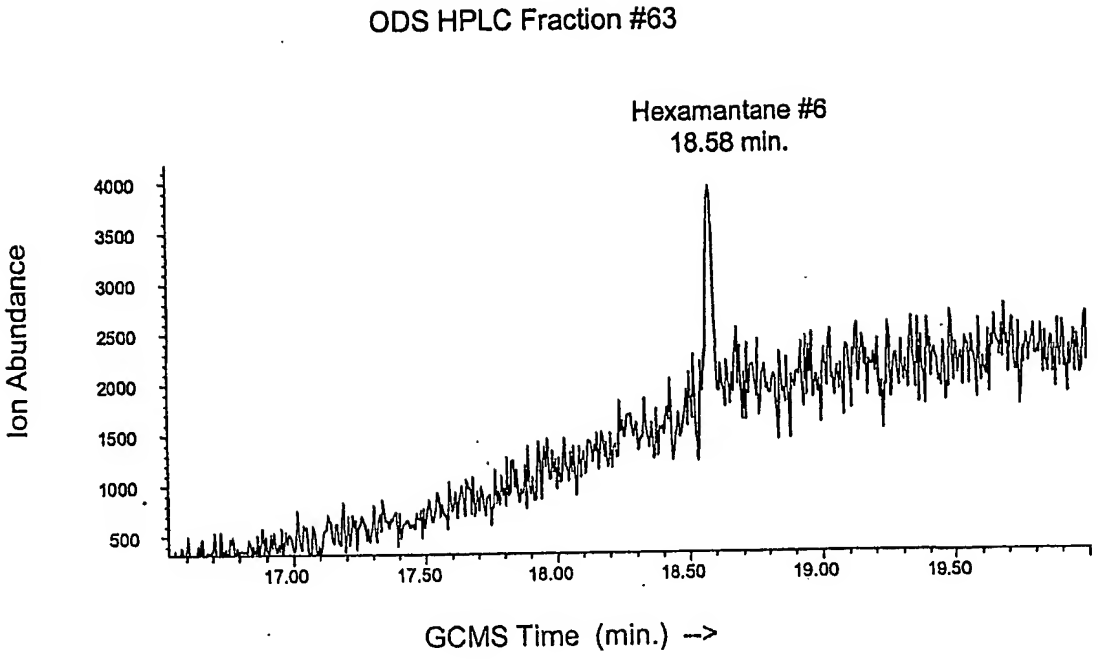

Mass Spectrum
Hexamantane # 10
@ 18.95 min.
M+
396
Ion Abundance
3000
2500
2000
1500
1000
500
0
198
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400

FIG. 49

A)


ODS HPLC Fraction #63
Hexamantane #6
18.58 min.
Ion Abundance
4000
3500
3000
2500
2000
1500
1000
500
17.00
17.50
18.00
18.50
19.00
19.50
GCMS Time (min.) -->

B)

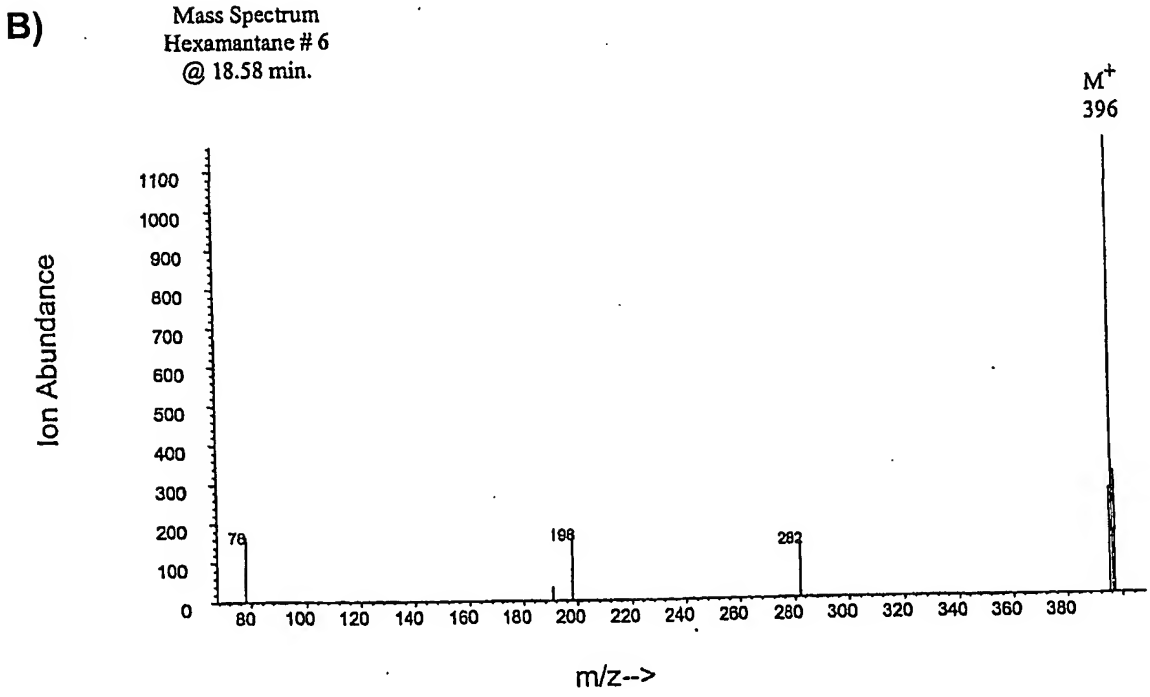
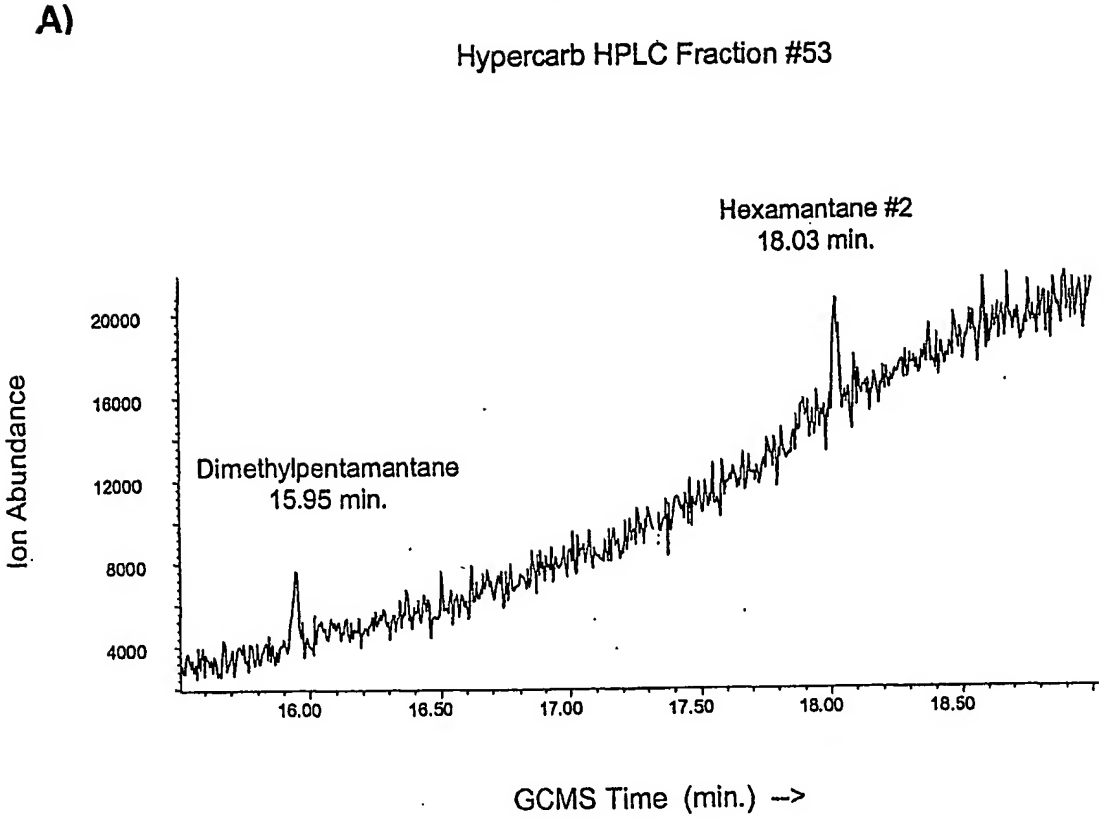

Mass Spectrum
Hexamantane # 6
@ 18.58 min.
M+
396
Ion Abundance
1100
1000
900
800
700
600
500
400
300
200
100
0
79
198
282
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
m/z-->

FIG. 50

A)


Hypercarb HPLC Fraction #53
Hexamantane #2
18.03 min.
Dimethylpentamantane
15.95 min.
Ion Abundance
20000
16000
12000
8000
4000
16.00
16.50
17.00
17.50
18.00
18.50
GCMS Time (min.) -->

B)

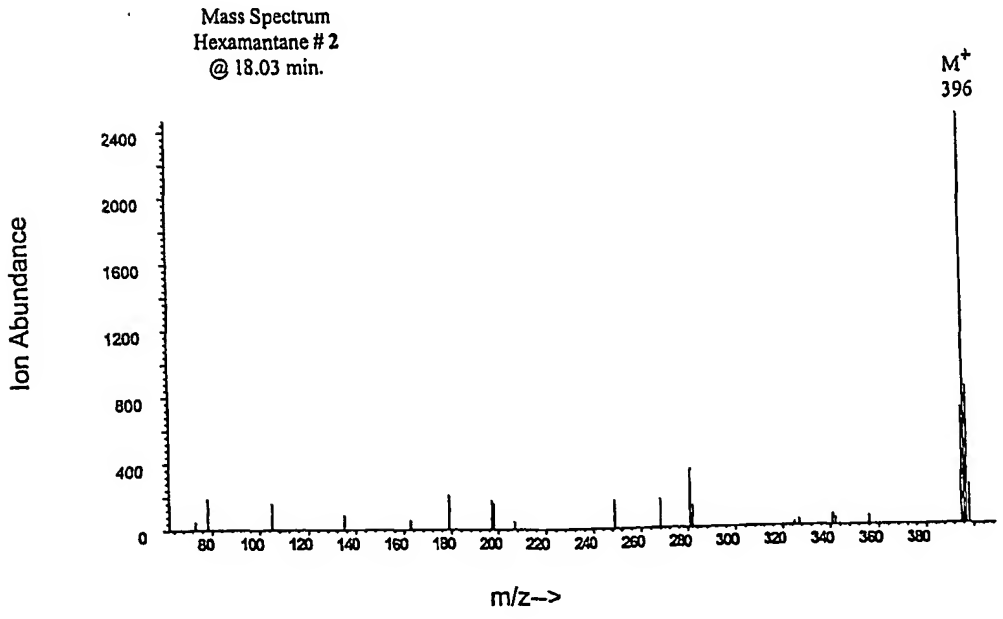
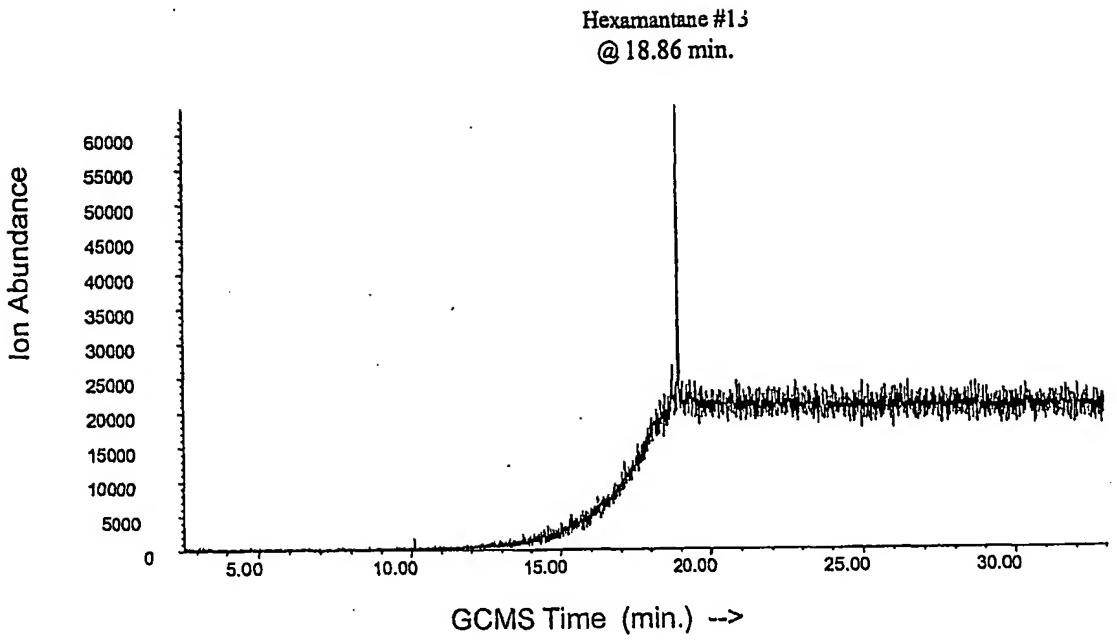

Mass Spectrum
Hexamantane # 2
@ 18.03 min.
M+
396
Ion Abundance
2400
2000
1600
1200
800
400
0
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
m/z-->

FIG. 51

A)


Hexamantane #13
@ 18.86 min.
Ion Abundance
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
5.00
10.00
15.00
20.00
25.00
30.00
GCMS Time (min.) -->

B)

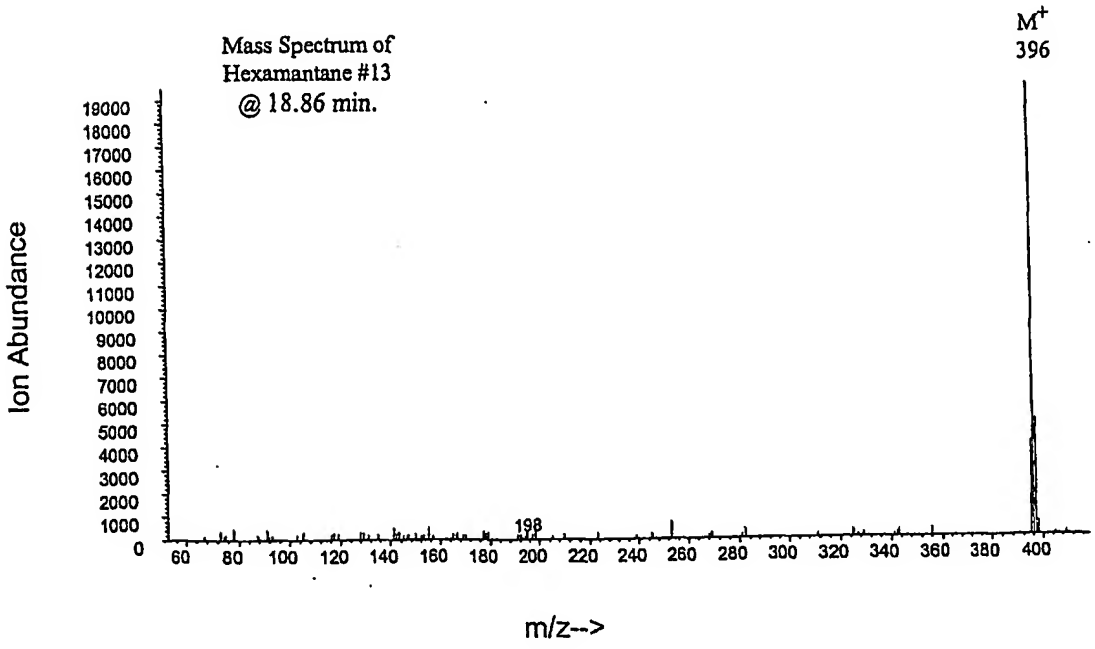
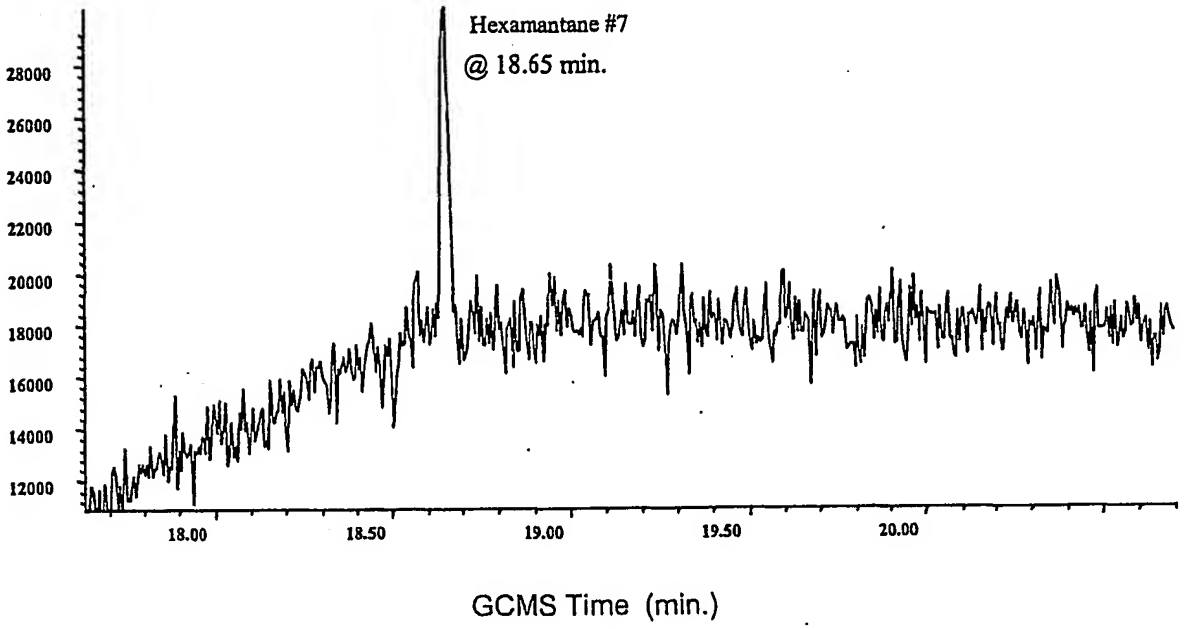

Mass Spectrum of
Hexamantane #13
@ 18.86 min.
M+
396
Ion Abundance
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
198
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
m/z-->

FIG. 52

A)


Hexamantane #7
@ 18.65 min.
28000
26000
24000
22000
20000
18000
16000
14000
12000
18.00
18.50
19.00
19.50
20.00
GCMS Time (min.)

B)

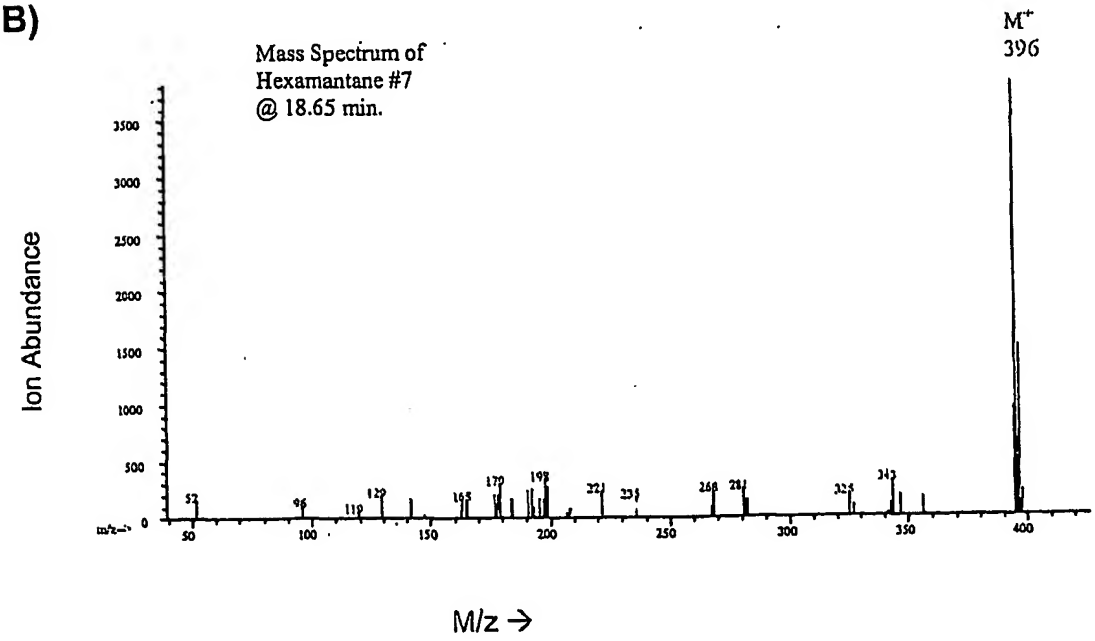
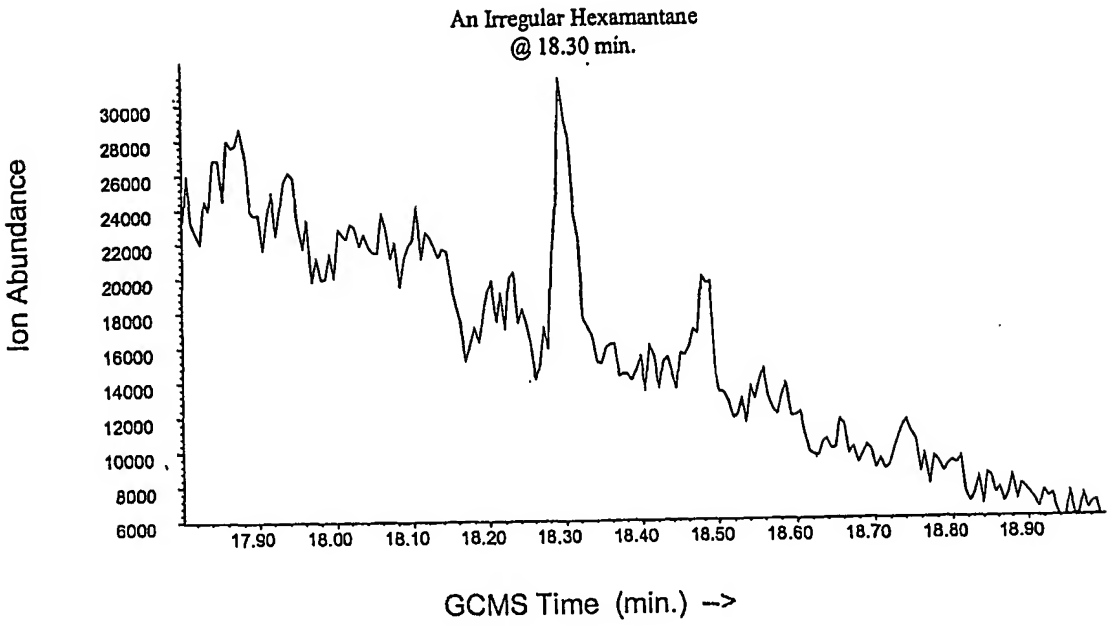

Mass Spectrum of
Hexamantane #7
@ 18.65 min.
M+
396
Ion Abundance
3500
3000
2500
2000
1500
1000
500
0
50
100
150
200
250
300
350
400
M/z →

FIG. 53

A)


An Irregular Hexamantane
@ 18.30 min.
Ion Abundance
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
17.90
18.00
18.10
18.20
18.30
18.40
18.50
18.60
18.70
18.80
18.90
GCMS Time (min.) -->

B)

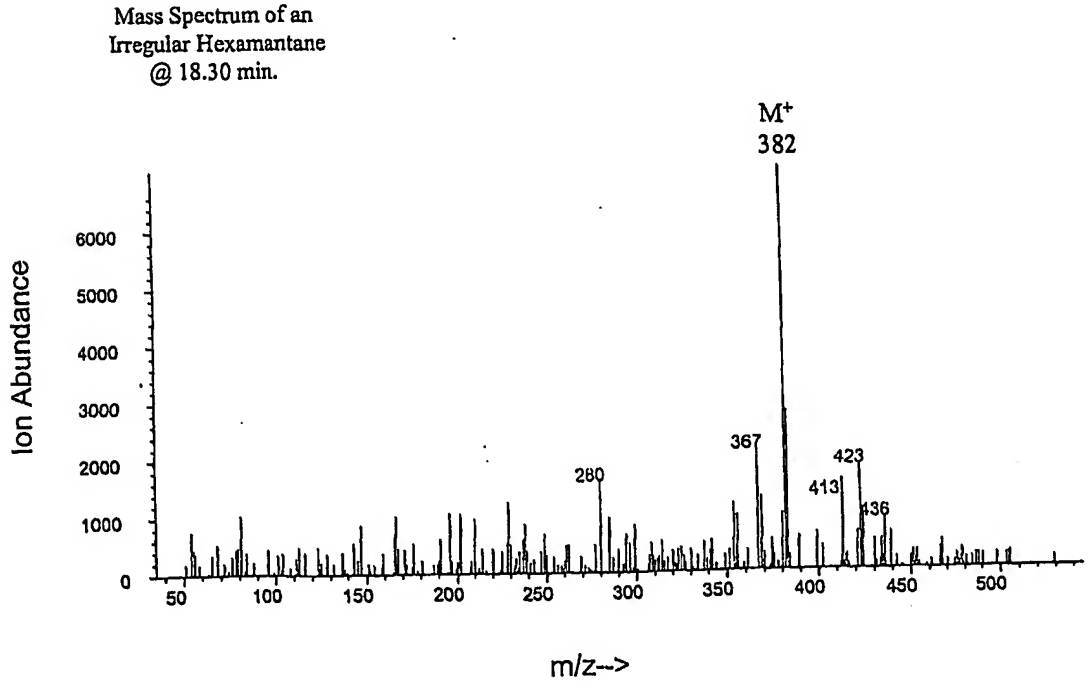
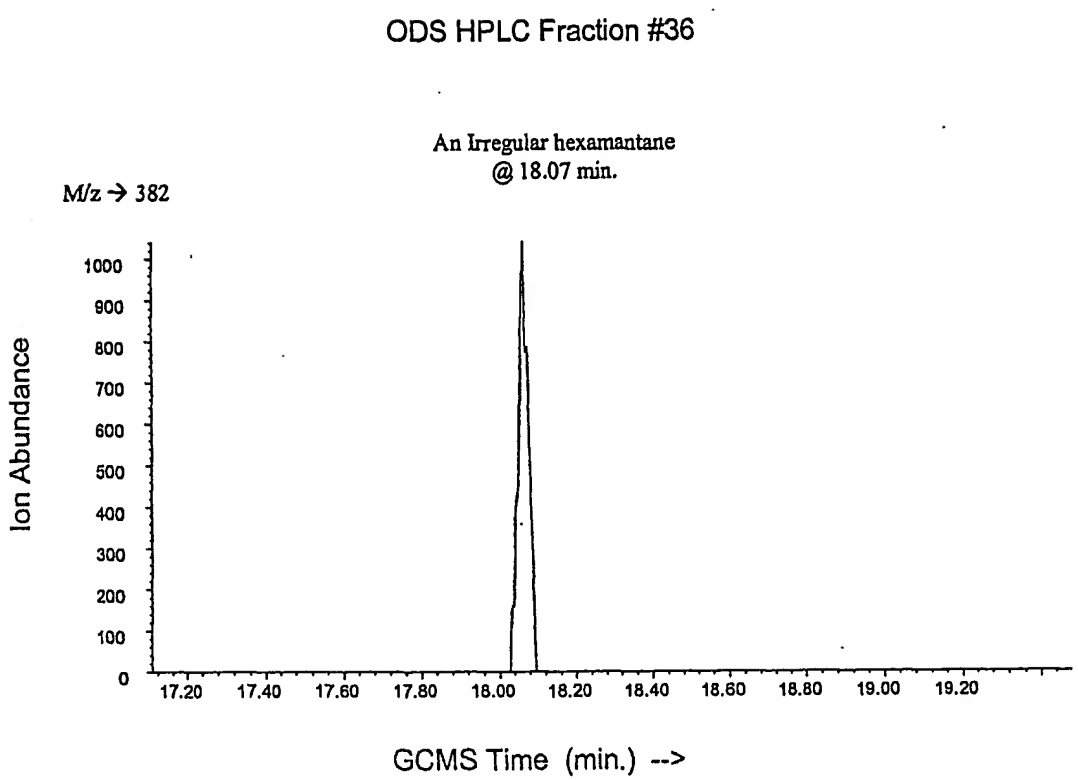

Mass Spectrum of an
Irregular Hexamantane
@ 18.30 min.
M+
382
Ion Abundance
6000
5000
4000
3000
2000
1000
0
367
280
423
413
436
50
100
150
200
250
300
350
400
450
500
m/z-->

FIG. 54

A)


ODS HPLC Fraction #36
An Irregular hexamantane
@ 18.07 min.
M/z → 382
Ion Abundance
1000
900
800
700
600
500
400
300
200
100
0
17.20
17.40
17.60
17.80
18.00
18.20
18.40
18.60
18.80
19.00
19.20
GCMS Time (min.) -->

B)

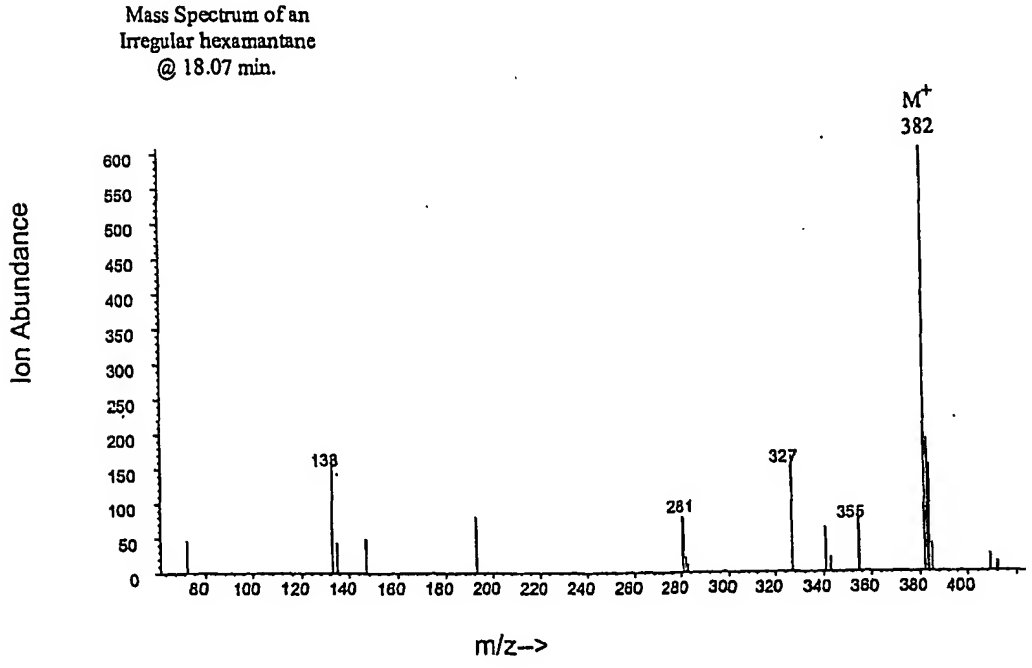
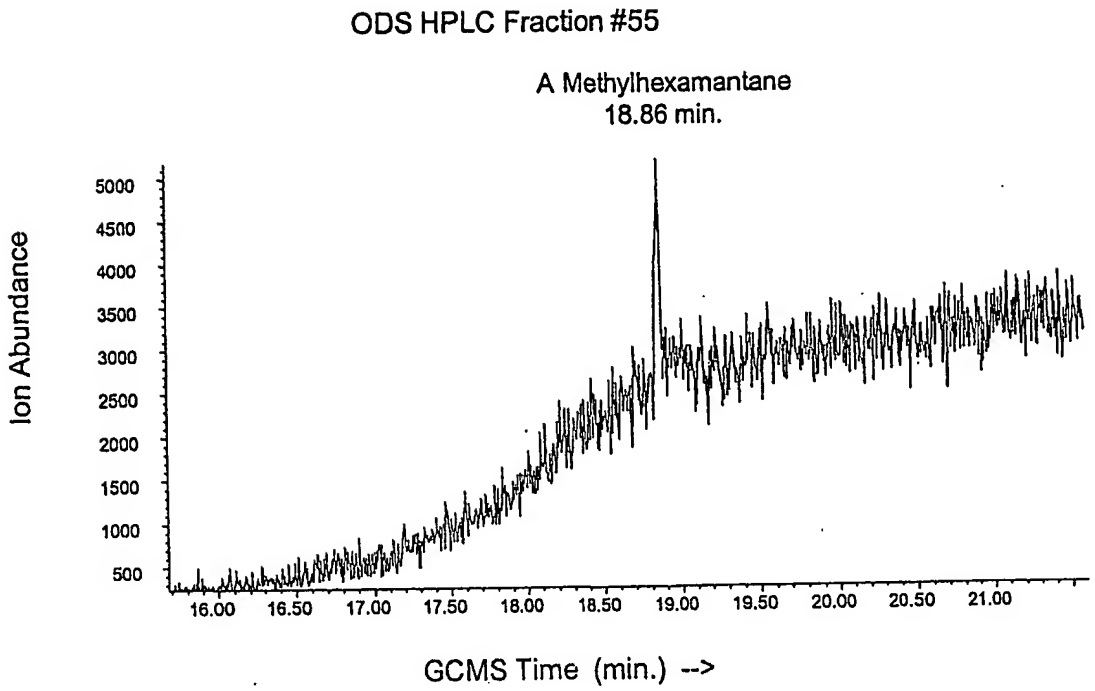

Mass Spectrum of an
Irregular hexamantane
@ 18.07 min.
M+
382
Ion Abundance
600
550
500
450
400
350
300
250
200
150
100
50
0
138
281
327
355
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
m/z-->

FIG. 55

A)


ODS HPLC Fraction #55
A Methylhexamantane
18.86 min.
Ion Abundance
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
16.00
16.50
17.00
17.50
18.00
18.50
19.00
19.50
20.00
20.50
21.00
GCMS Time (min.) -->

B)

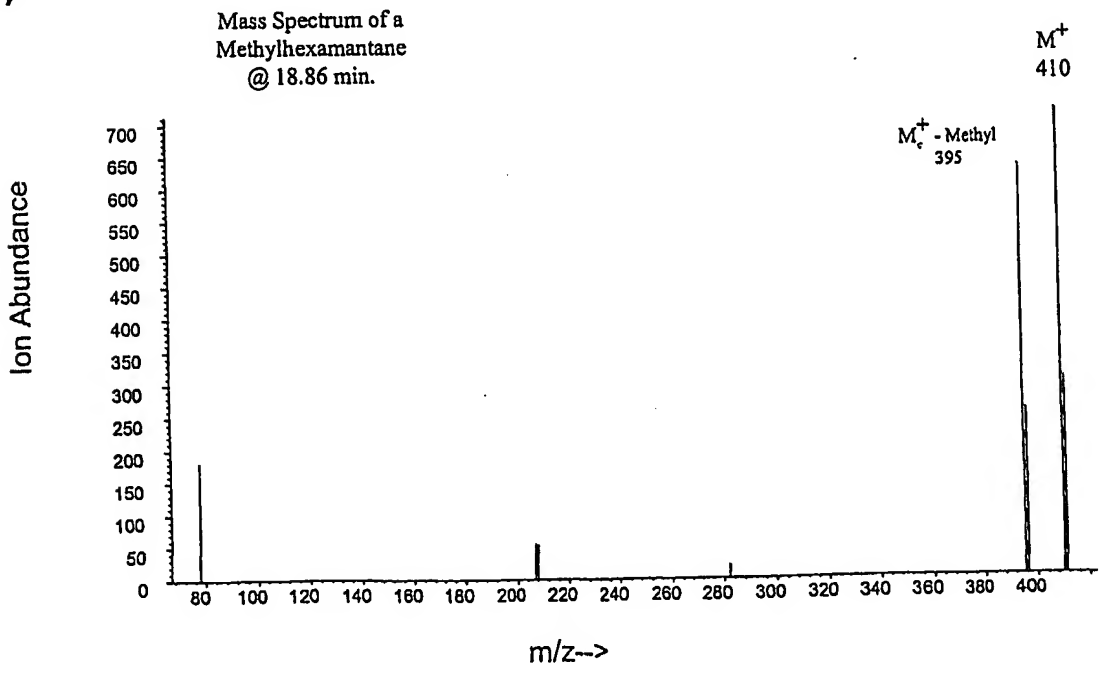

Mass Spectrum of a
Methylhexamantane
@ 18.86 min.
M+
410
M+ - Methyl
395
Ion Abundance
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
m/z-->

FIG. 56

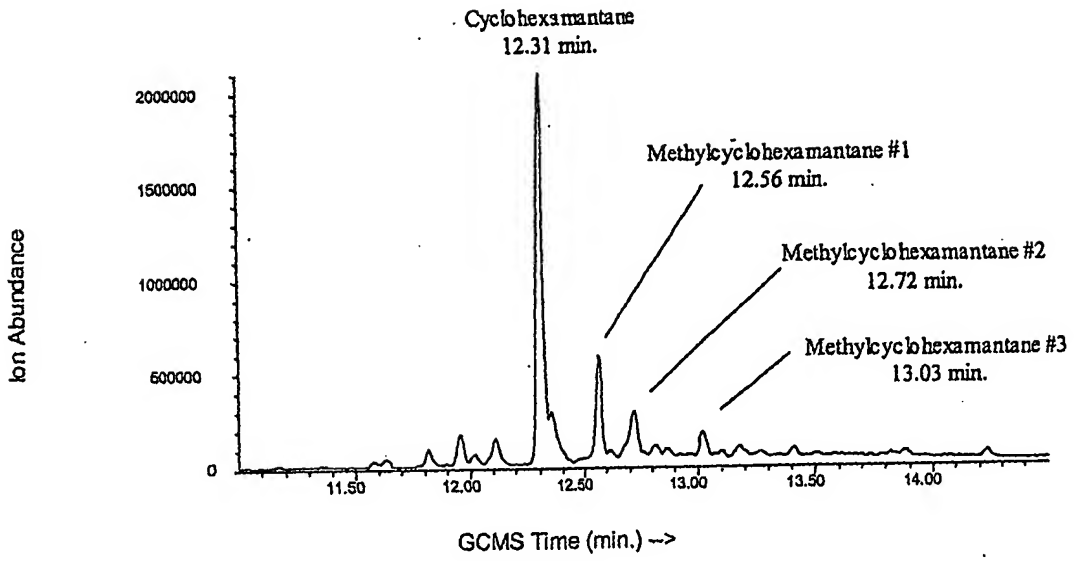
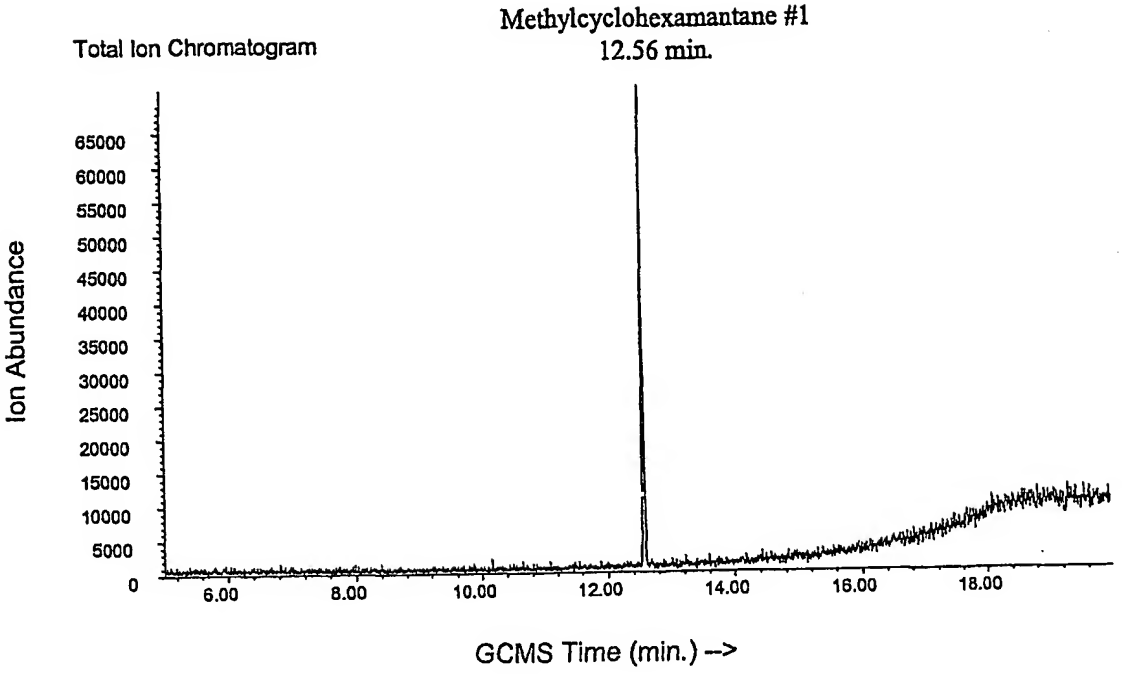

Cyclohexamantane
12.31 min.
Methylcyclohexamantane #1
12.56 min.
Methylcyclohexamantane #2
12.72 min.
Methylcyclohexamantane #3
13.03 min.
Ion Abundance
2000000
1500000
1000000
500000
0
11.50
12.00
12.50
13.00
13.50
14.00
GCMS Time (min.) -->

FIG. 57

A)


Methylcyclohexamantane #1
12.56 min.
Total Ion Chromatogram
Ion Abundance
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
6.00
8.00
10.00
12.00
14.00
16.00
18.00
GCMS Time (min.) -->

B)

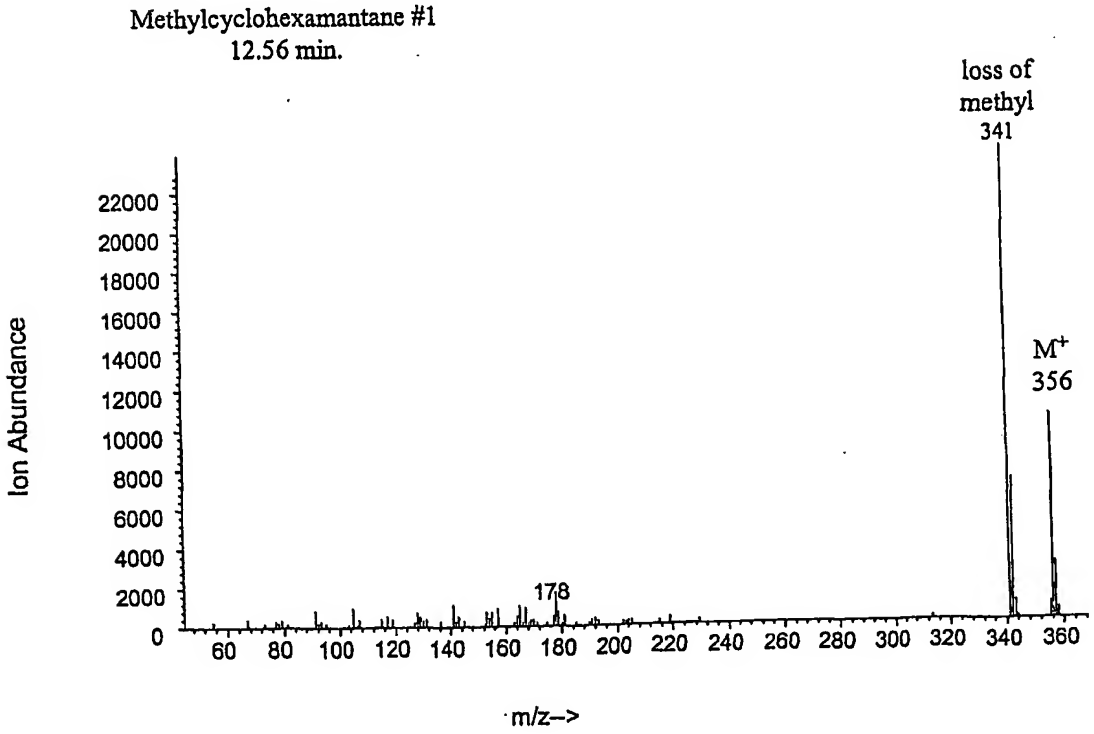
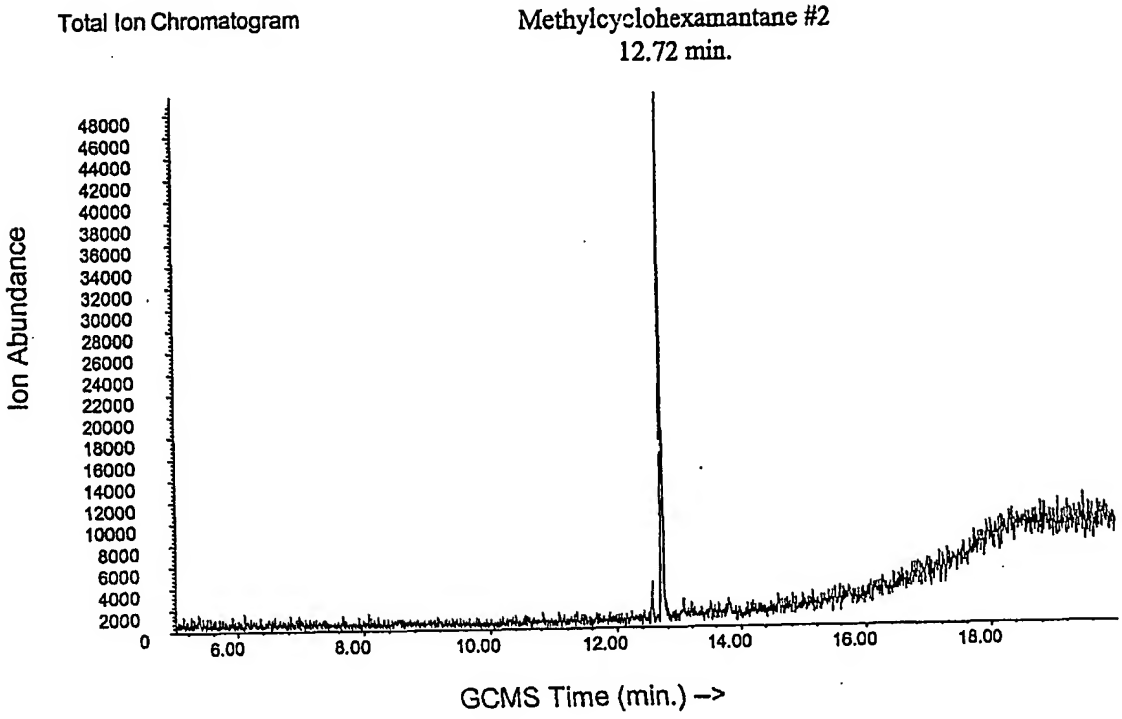

Methylcyclohexamantane #1
12.56 min.
loss of
methyl
341
M+
356
178
Ion Abundance
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
m/z-->

FIG. 58

A)


Total Ion Chromatogram
Methylcyclohexamantane #2
12.72 min.
Ion Abundance
48000
46000
44000
42000
40000
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
6.00
8.00
10.00
12.00
14.00
16.00
18.00
GCMS Time (min.) -->

B)

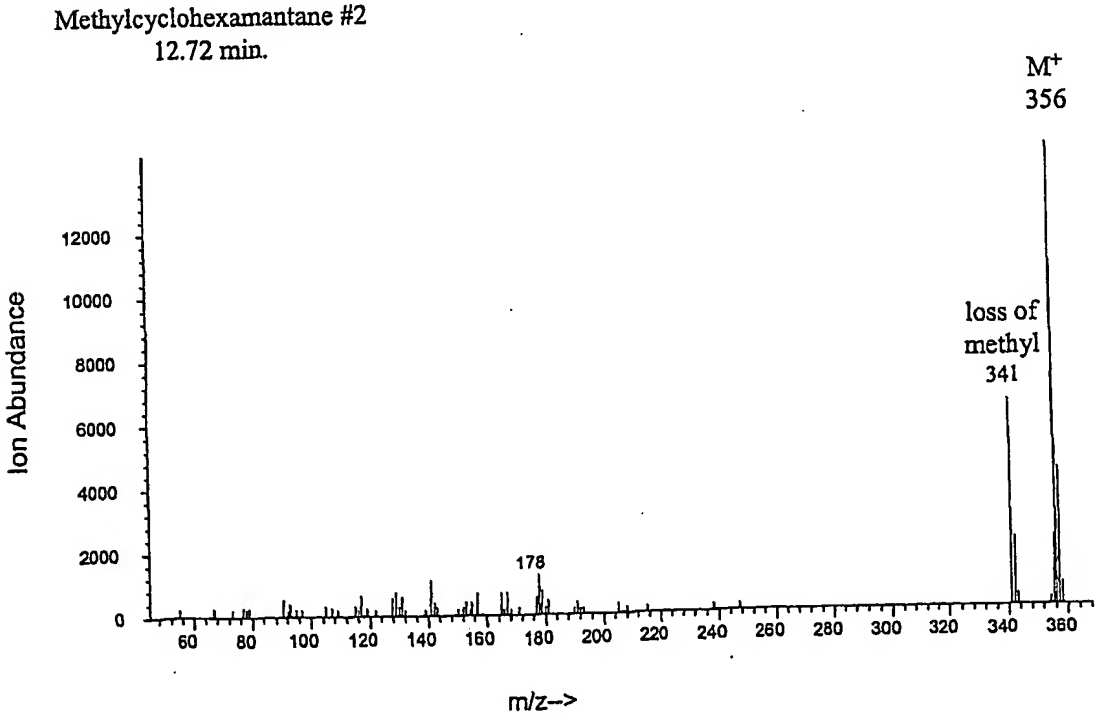
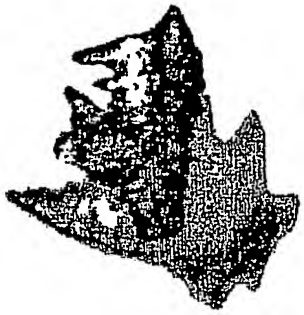

Methylcyclohexamantane #2
12.72 min.
M+
356
loss of
methyl
341
178
Ion Abundance
12000
10000
8000
6000
4000
2000
0
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
m/z-->

FIG. 59



Methylcyclohexamantane
HPLC 37 Fraction 19-21

FIG. 60

Methylcyclohexamantane
HPLC 37 Fraction 23

FIG. 61

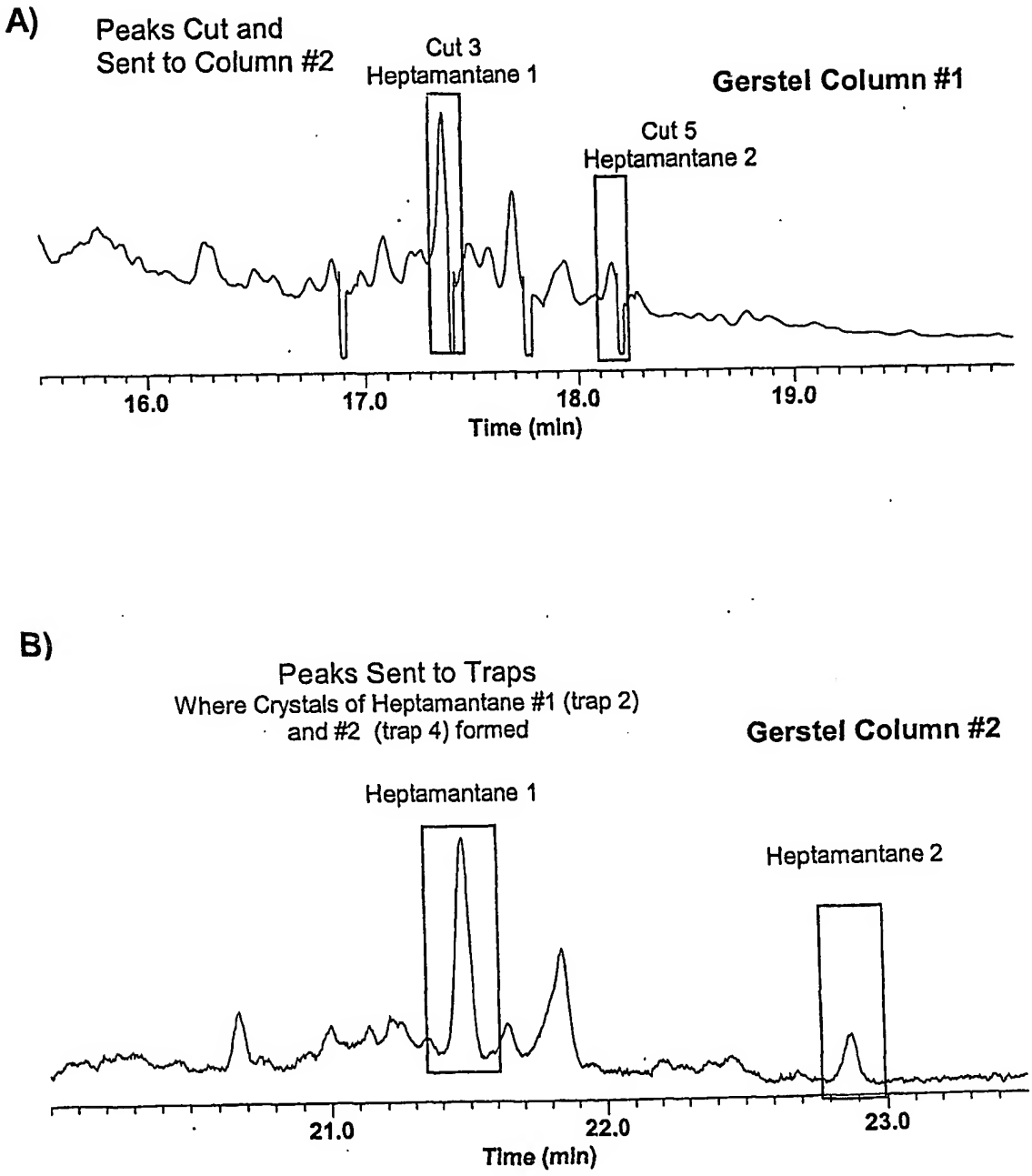
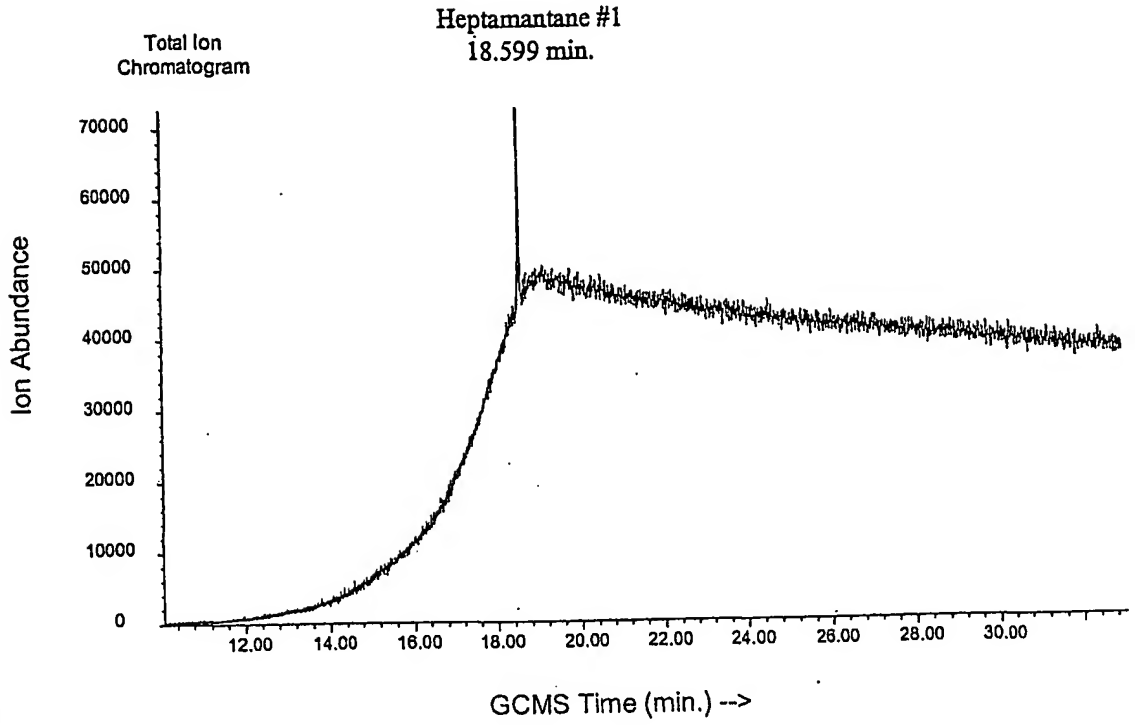

A)
Peaks Cut and
Sent to Column #2
Cut 3
Heptamantane 1
Gerstel Column #1
Cut 5
Heptamantane 2
16.0
17.0
18.0
19.0
Time (min)
B)
Peaks Sent to Traps
Where Crystals of Heptamantane #1 (trap 2)
and #2 (trap 4) formed
Gerstel Column #2
Heptamantane 1
Heptamantane 2
21.0
22.0
23.0
Time (min)

FIG. 62

A)


Heptamantane #1
18.599 min.
Total Ion
Chromatogram
Ion Abundance
70000
60000
50000
40000
30000
20000
10000
0
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
28.00
30.00
GCMS Time (min.) -->

B)

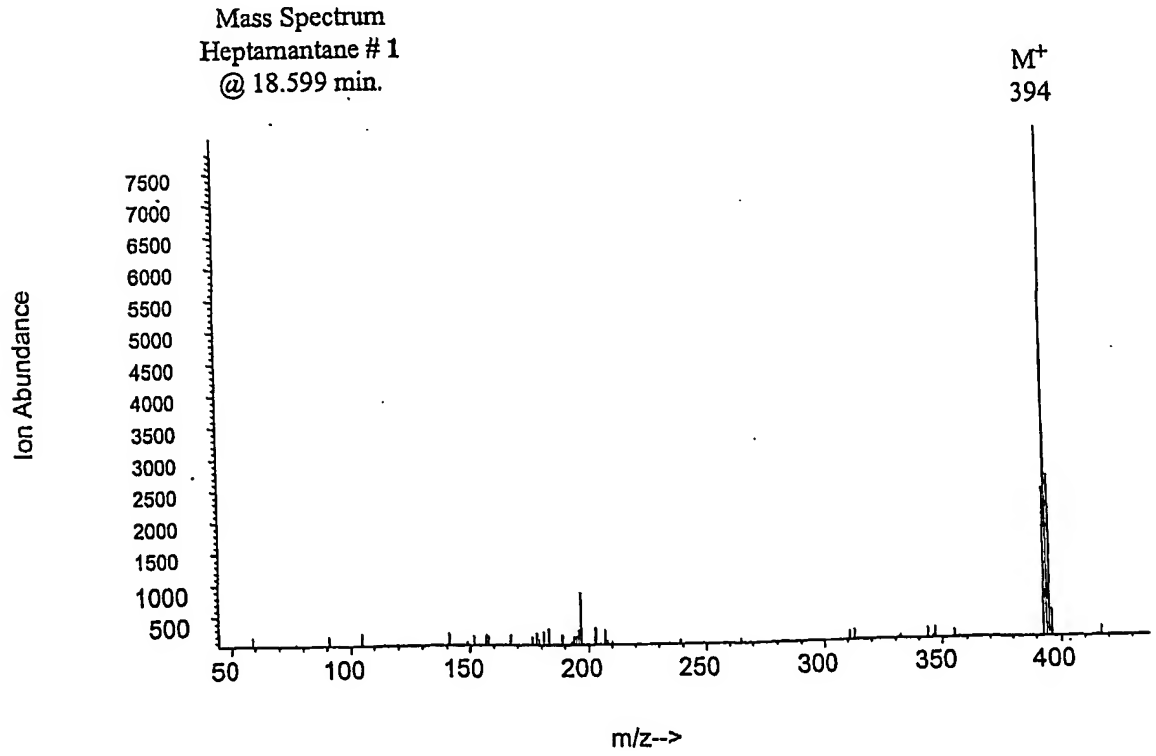
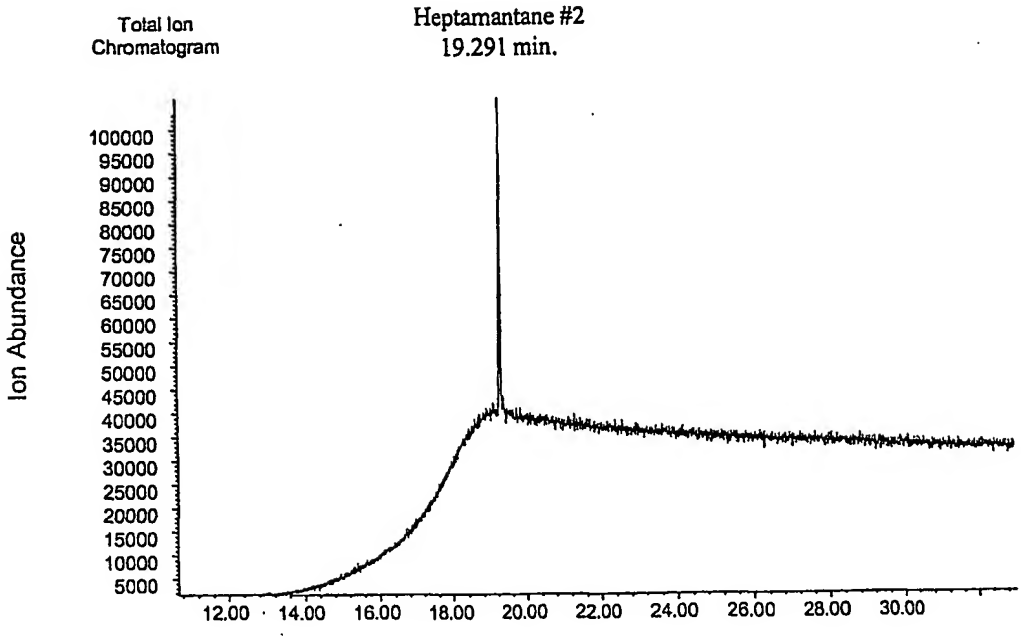

Mass Spectrum
Heptamantane # 1
@ 18.599 min.
M+
394
Ion Abundance
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
50
100
150
200
250
300
350
400
m/z-->

FIG. 63

A)


Total Ion Chromatogram
Heptamantane #2
19.291 min.
Ion Abundance
100000
95000
90000
85000
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
28.00
30.00
GCMS Time (min.) -->

B)

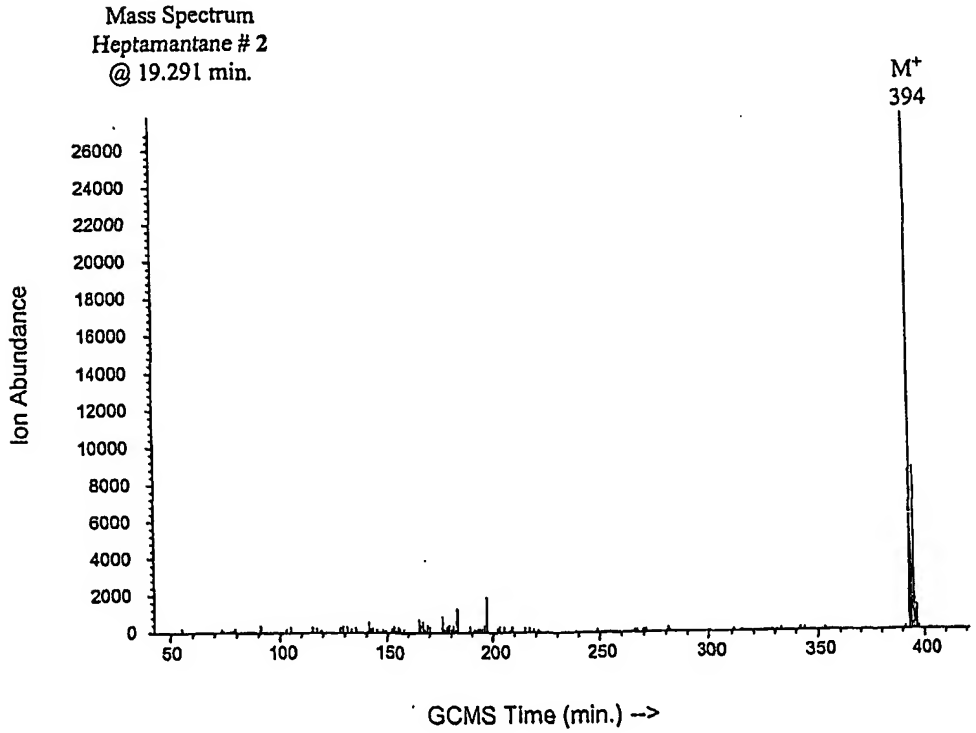
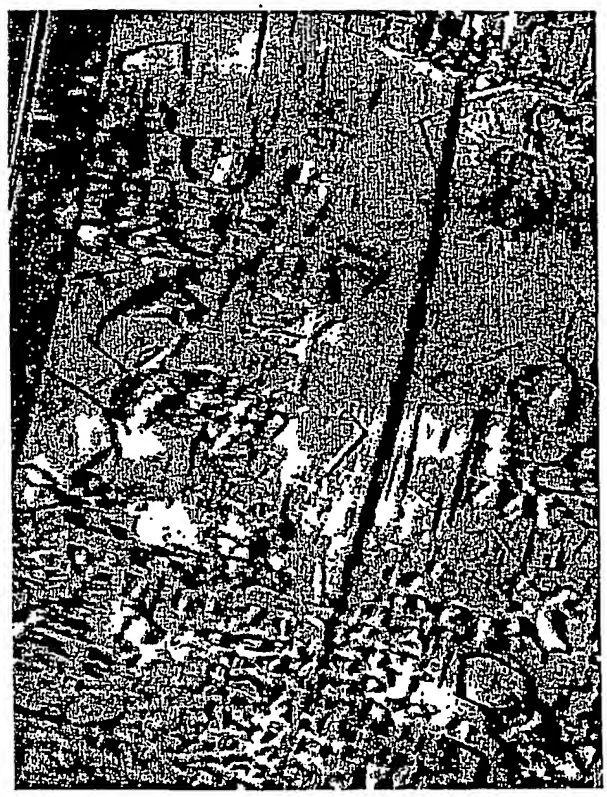
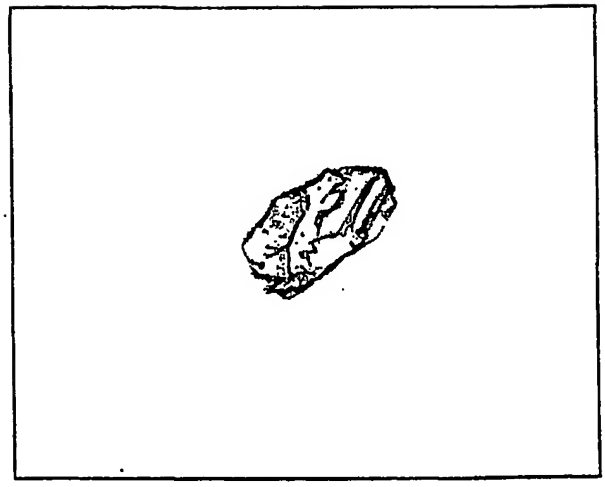

Mass Spectrum
Heptamantane # 2
@ 19.291 min.
M+
394
Ion Abundance
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
50
100
150
200
250
300
350
400
GCMS Time (min.) -->

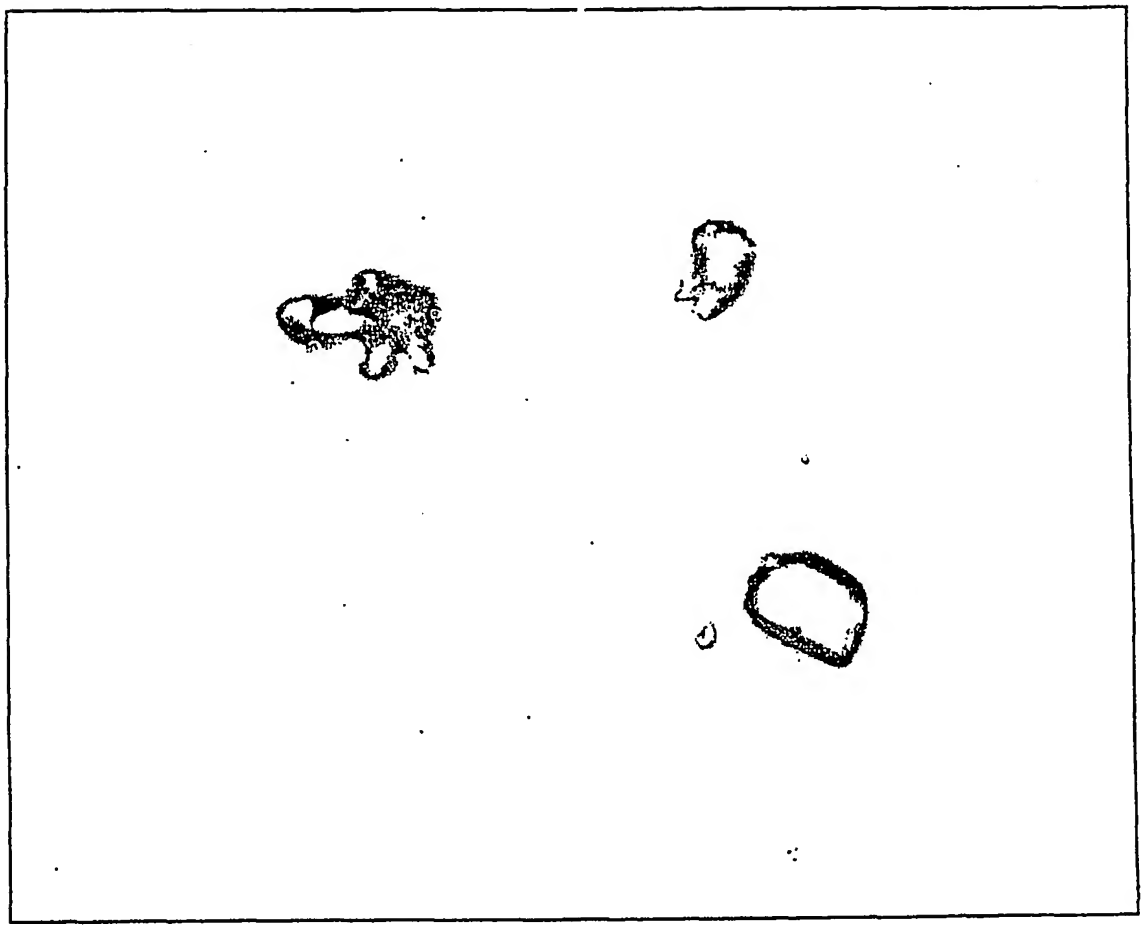
FIG. 64





Heptamantane #1 Crystals

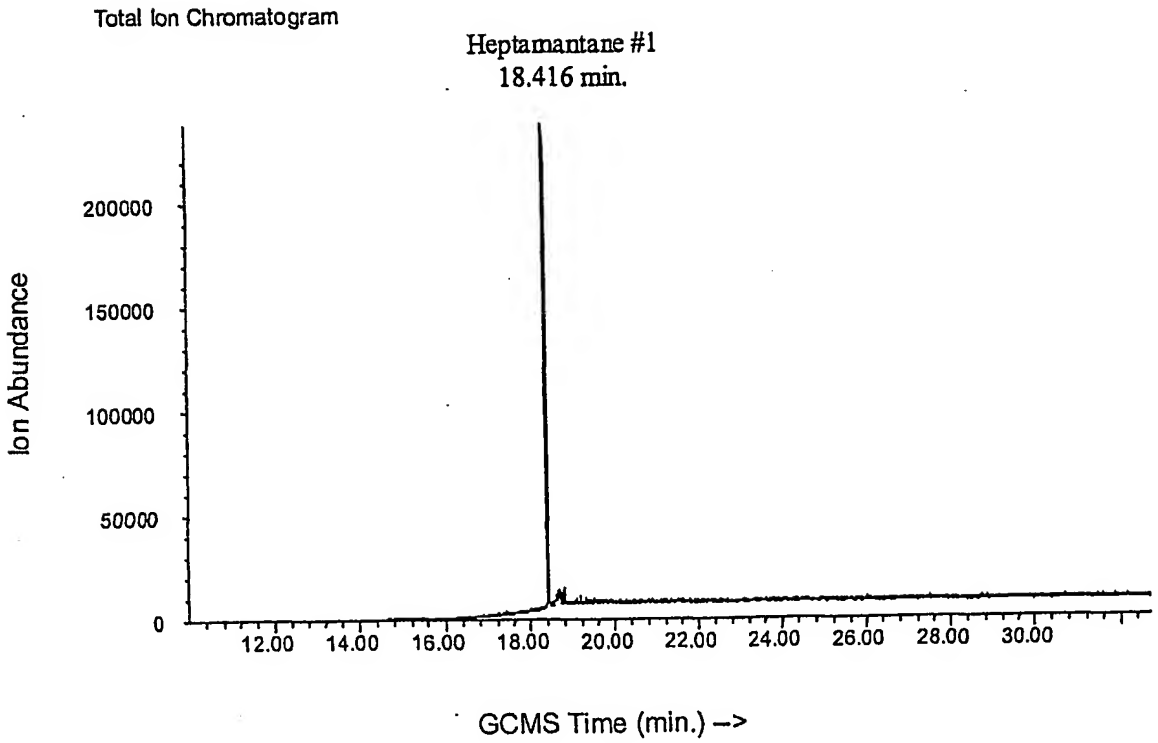
FIG. 65



Heptamantane #2
Crystals

FIG. 66

A)


Total Ion Chromatogram
Heptamantane #1
18.416 min.
Ion Abundance
200000
150000
100000
50000
0
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
28.00
30.00
GCMS Time (min.) -->

B)

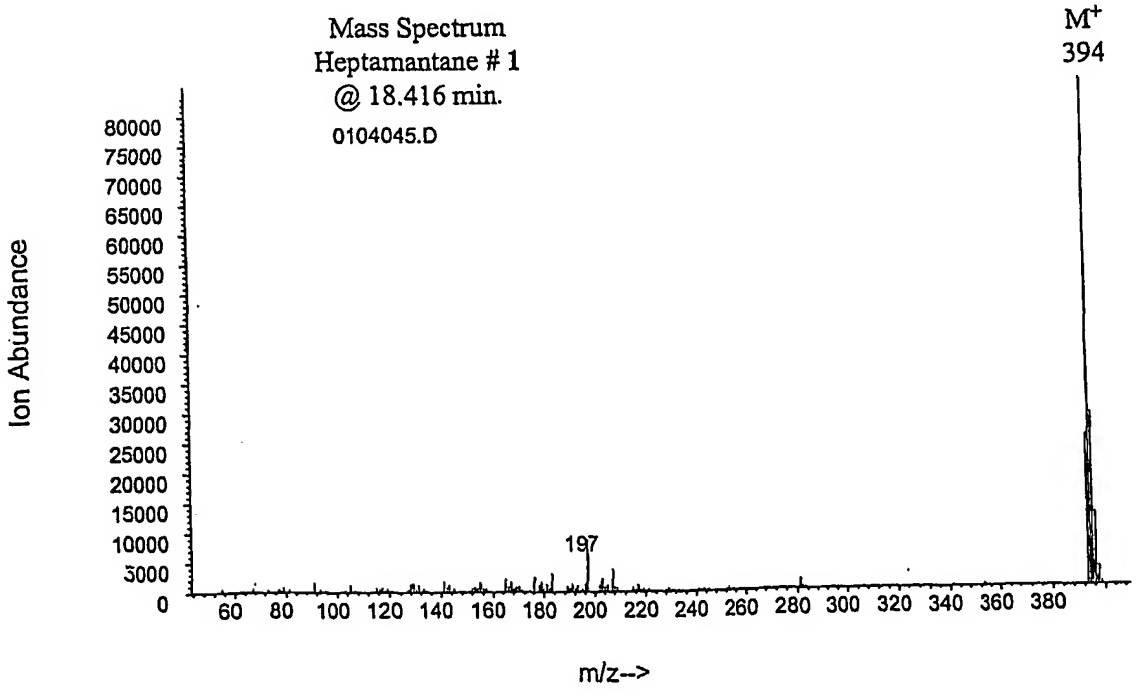
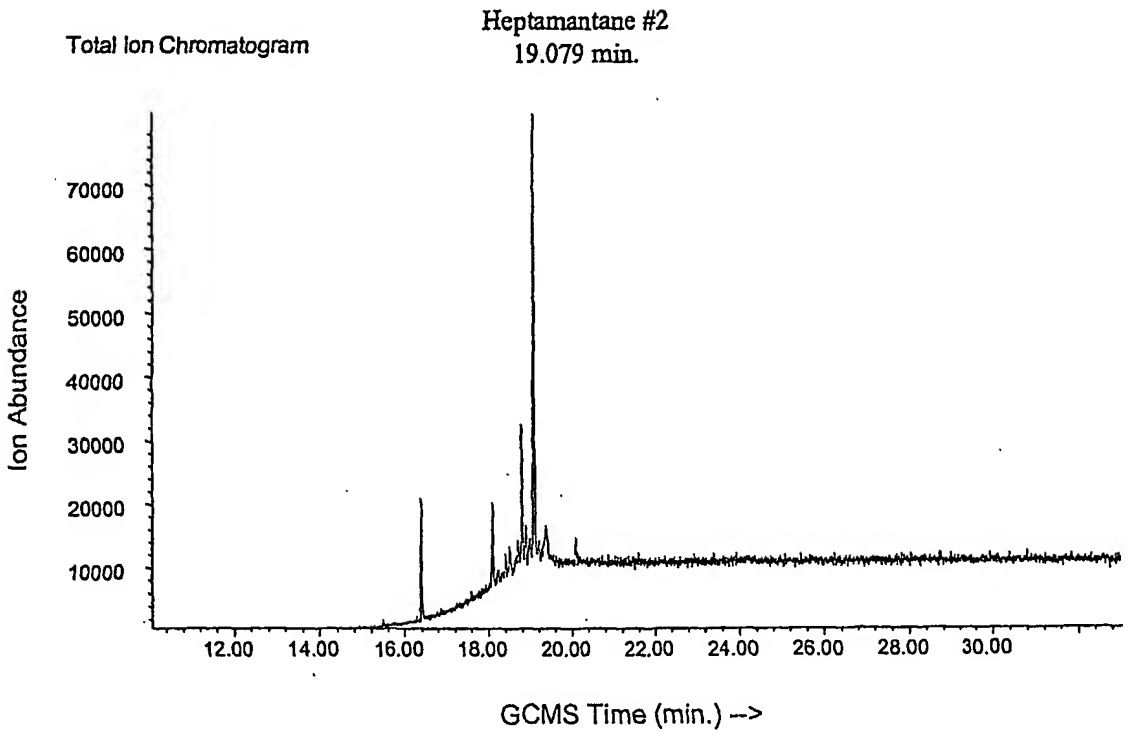

Mass Spectrum
Heptamantane # 1
@ 18.416 min.
0104045.D
M+
394
Ion Abundance
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
3000
0
197
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
m/z-->

FIG. 67

A)


Heptamantane #2
19.079 min.
Total Ion Chromatogram
Ion Abundance
70000
60000
50000
40000
30000
20000
10000
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
28.00
30.00
GCMS Time (min.) -->

B)

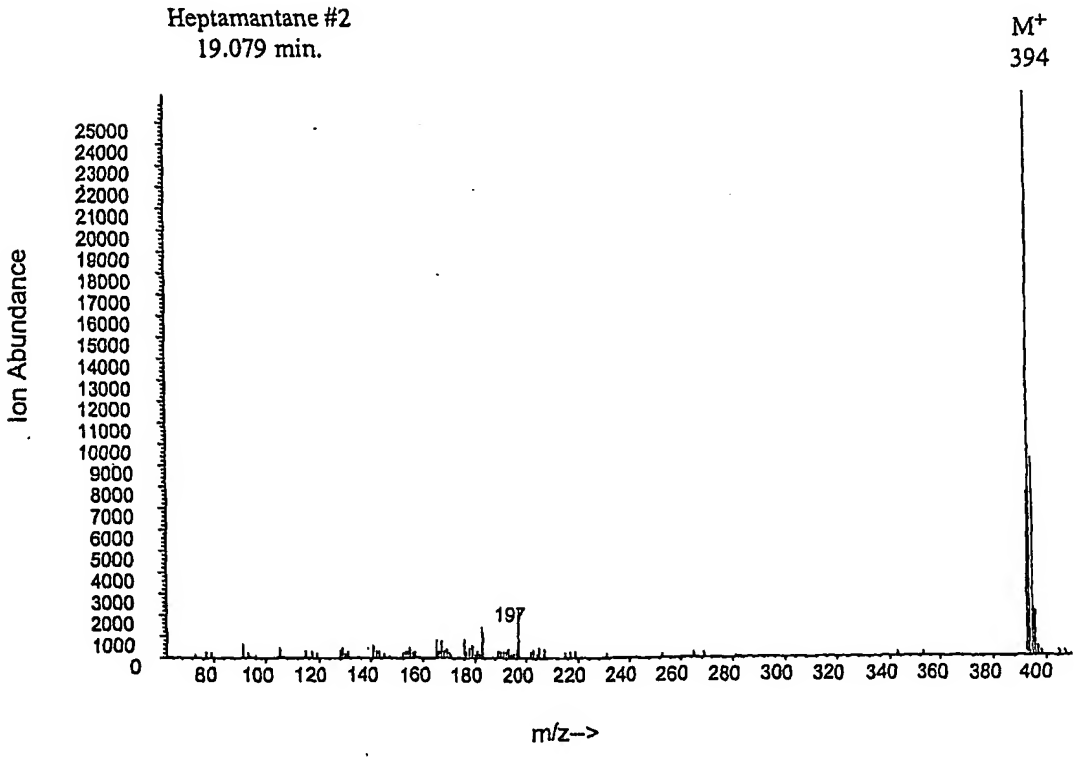
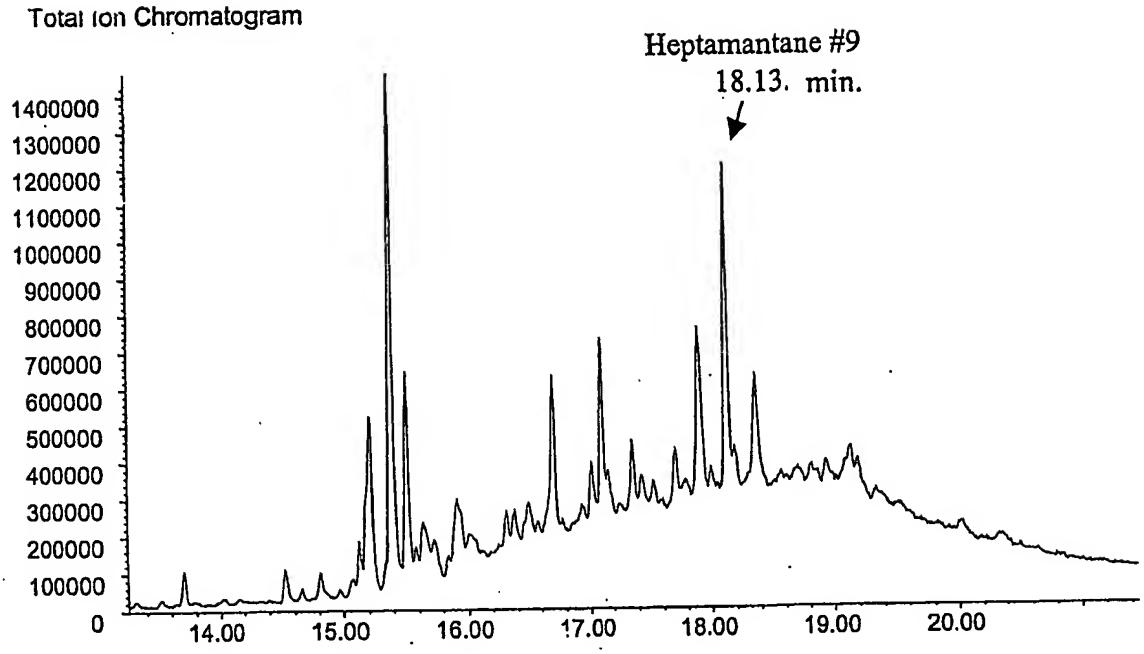

Heptamantane #2
19.079 min.
M+
394
Ion Abundance
25000
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
197
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
m/z-->

FIG. 68

A)


Total Ion Chromatogram
Heptamantane #9
18.13. min.
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
14.00
15.00
16.00
17.00
18.00
19.00
20.00

B)

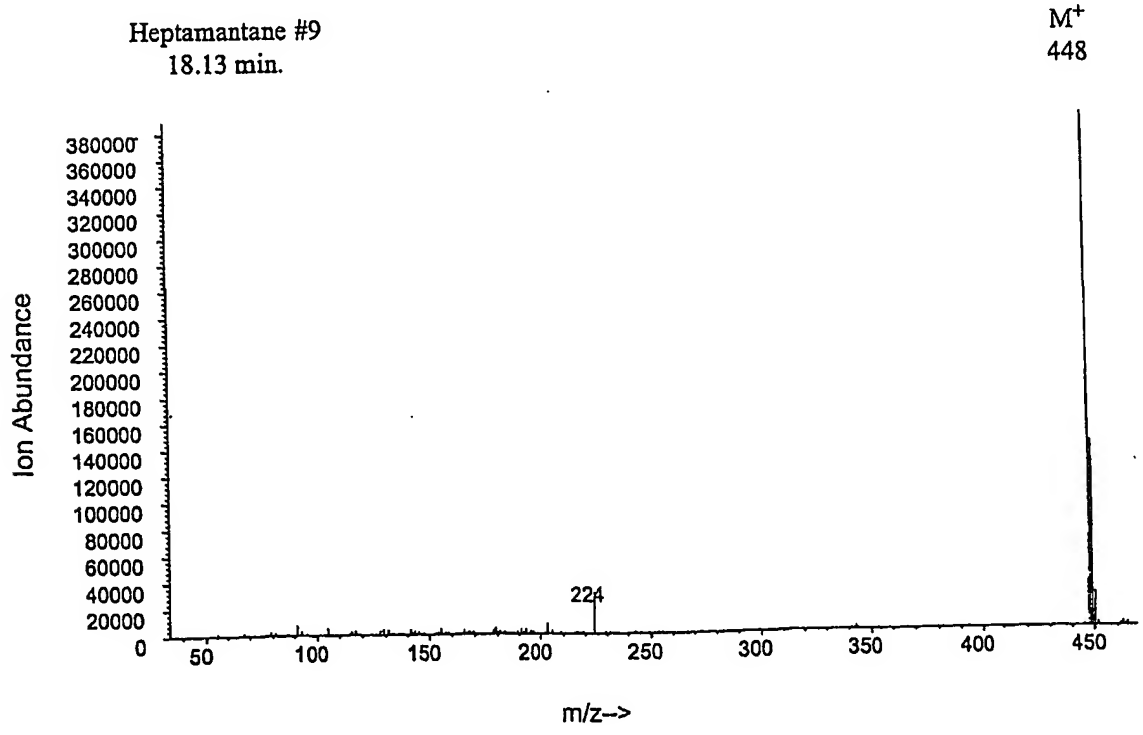
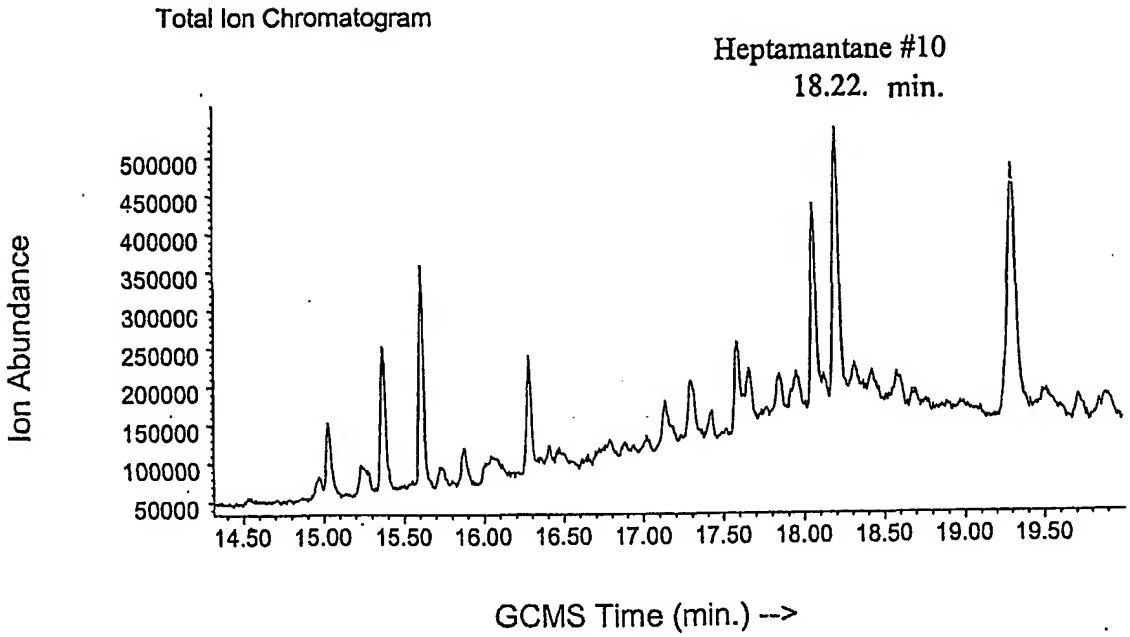

Heptamantane #9
18.13 min.
M+
448
Ion Abundance
380000
360000
340000
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
224
50
100
150
200
250
300
350
400
450
m/z-->

FIG. 69

A)


Total Ion Chromatogram
Heptamantane #10
18.22. min.
Ion Abundance
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
14.50
15.00
15.50
16.00
16.50
17.00
17.50
18.00
18.50
19.00
19.50
GCMS Time (min.) -->

B)

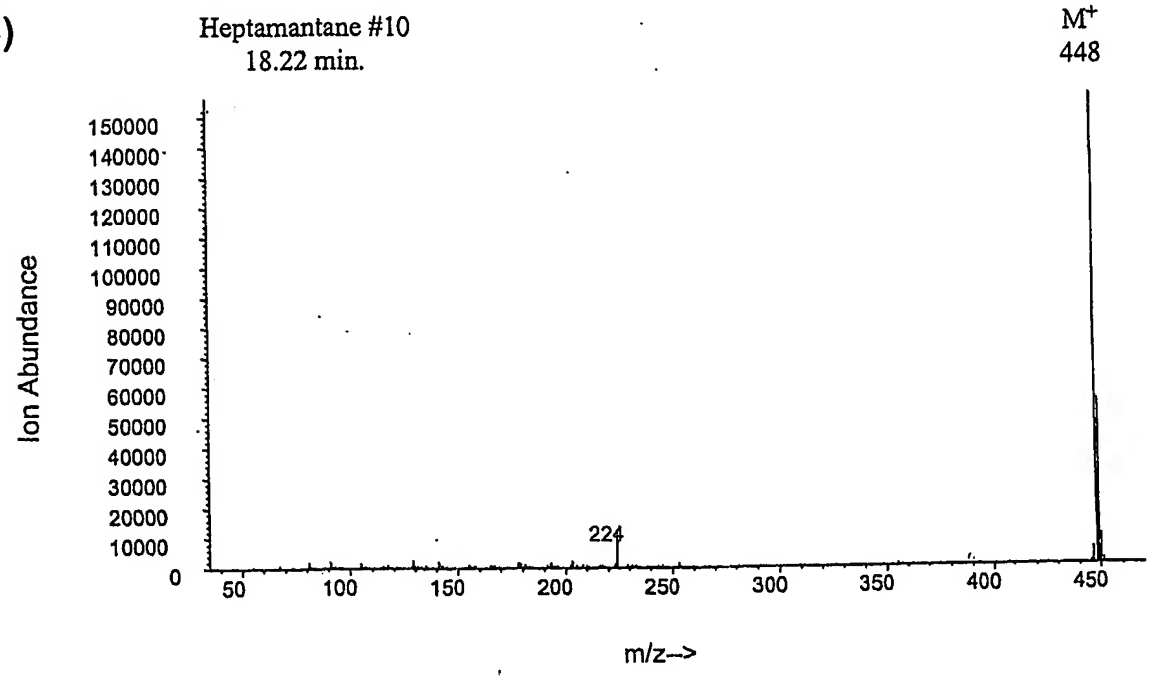
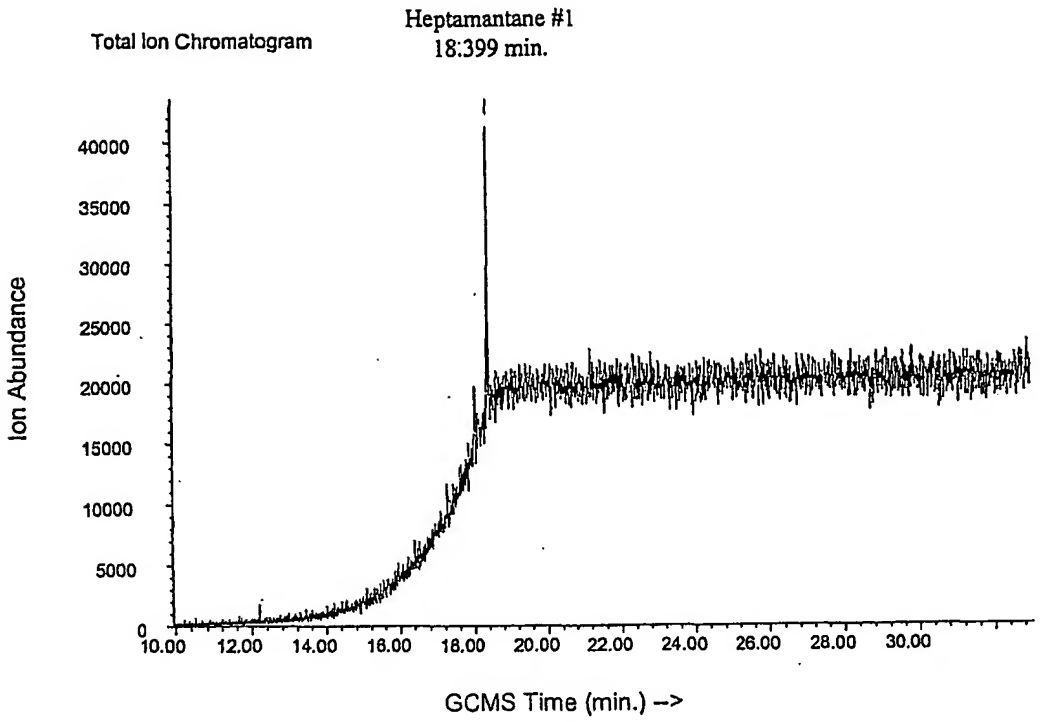

Heptamantane #10
18.22 min.
M+
448
Ion Abundance
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
224
50
100
150
200
250
300
350
400
450
m/z-->

FIG. 70

A)


Total Ion Chromatogram
Heptamantane #1
18.399 min.
Ion Abundance
40000
35000
30000
25000
20000
15000
10000
5000
0
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
28.00
30.00
GCMS Time (min.) -->

B)

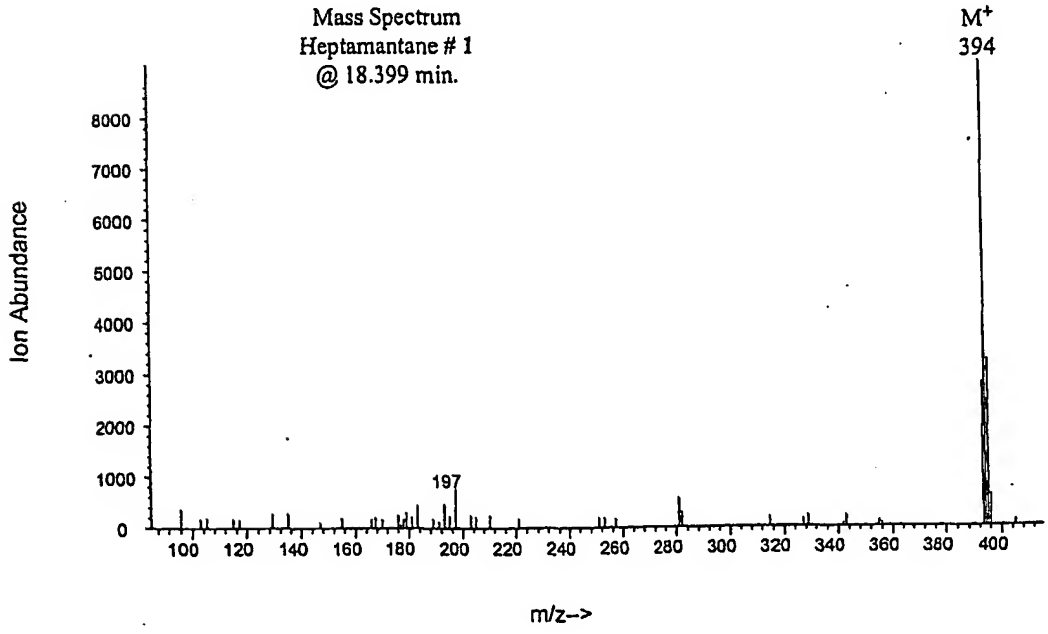
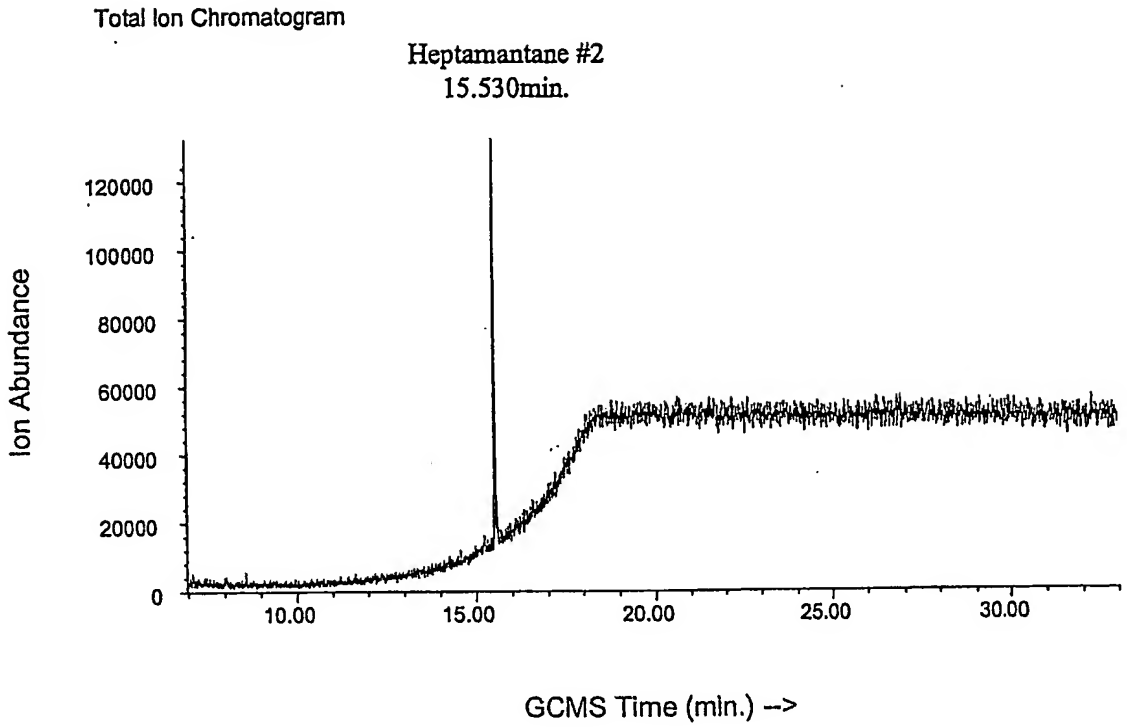

Mass Spectrum
Heptamantane # 1
@ 18.399 min.
M+
394
197
Ion Abundance
8000
7000
6000
5000
4000
3000
2000
1000
0
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
m/z-->

FIG. 71

A)


Total Ion Chromatogram
Heptamantane #2
15.530min.
Ion Abundance
120000
100000
80000
60000
40000
20000
0
10.00
15.00
20.00
25.00
30.00
GCMS Time (min.) -->

B)

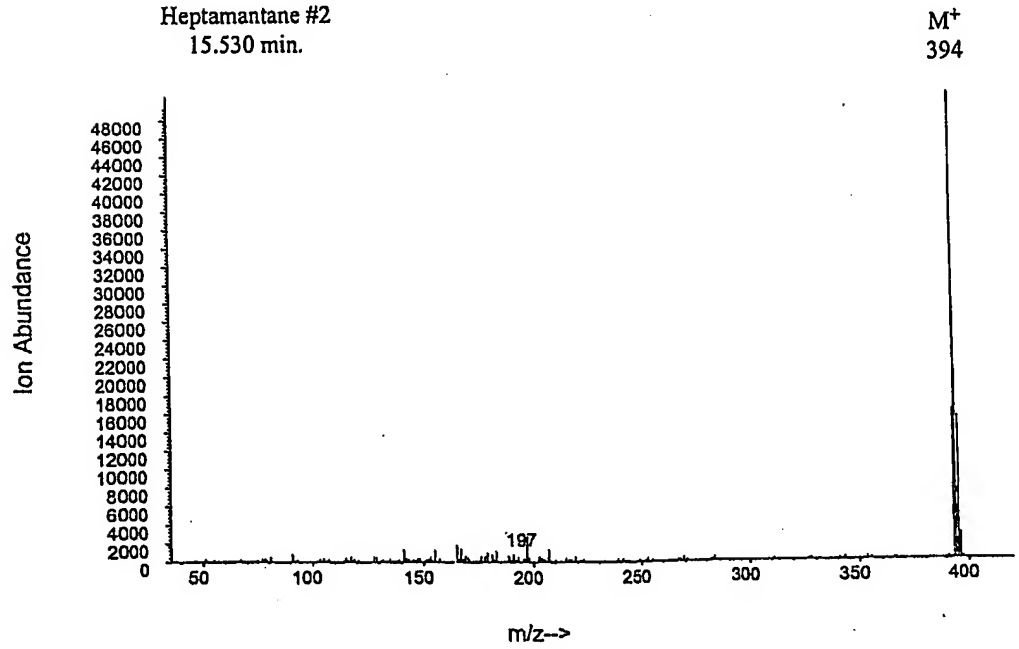

Heptamantane #2
15.530 min.
M+
394
Ion Abundance
48000
46000
44000
42000
40000
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
197
50
100
150
200
250
300
350
400
m/z-->

FIG. 72

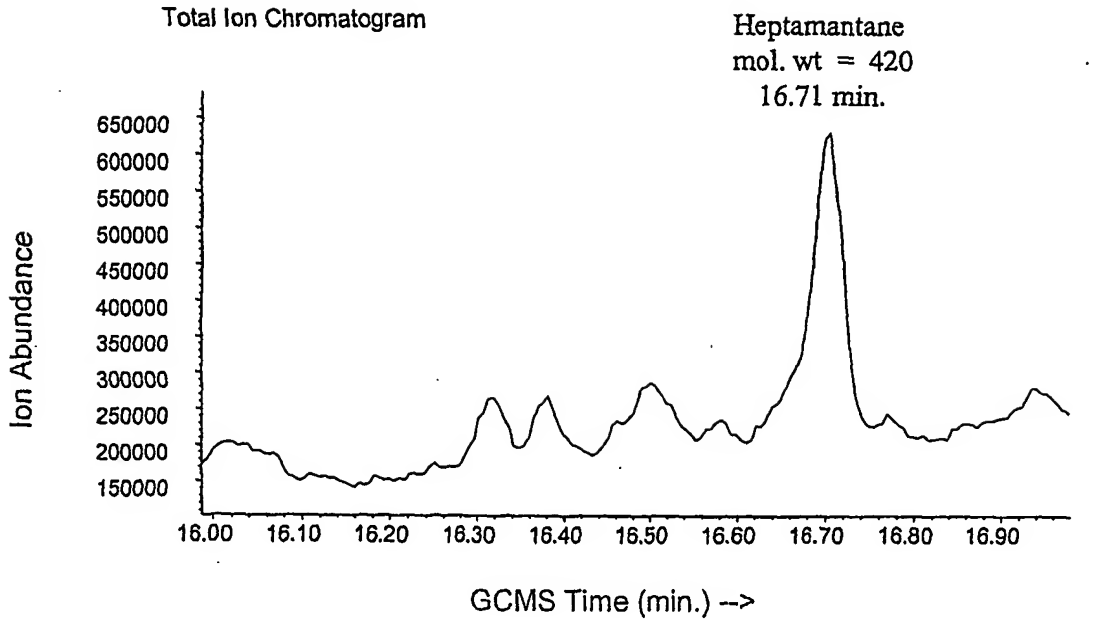

Total Ion Chromatogram
Heptamantane
mol. wt = 420
16.71 min.
Ion Abundance
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
16.00
16.10
16.20
16.30
16.40
16.50
16.60
16.70
16.80
16.90
GCMS Time (min.) -->

FIG. 73

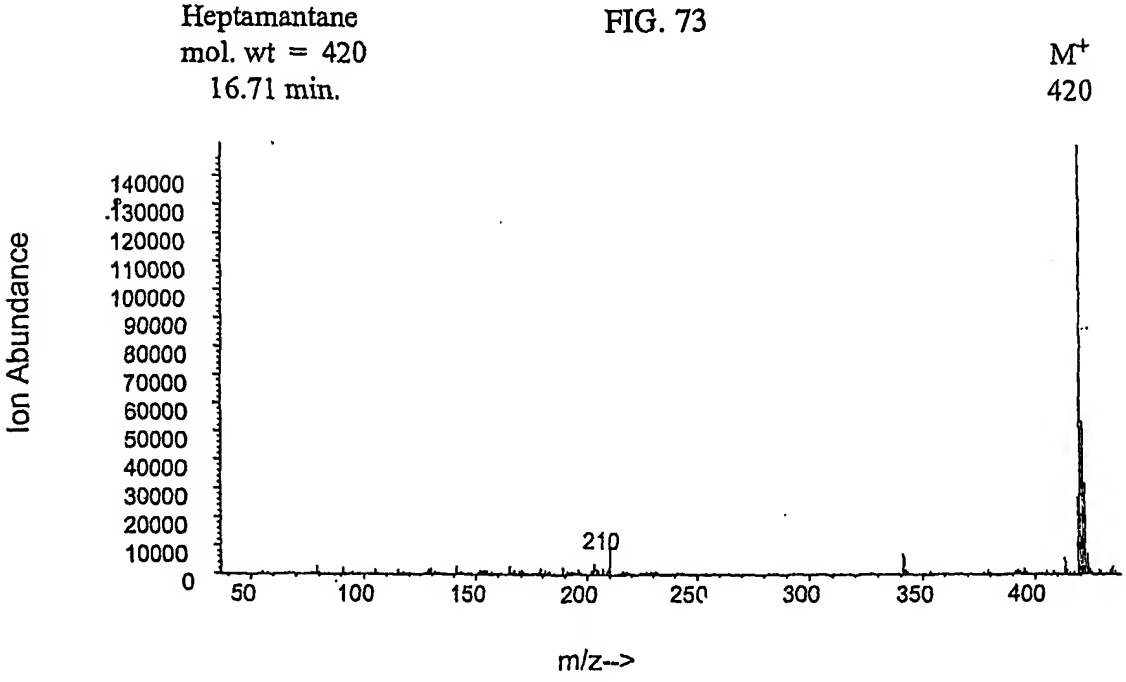
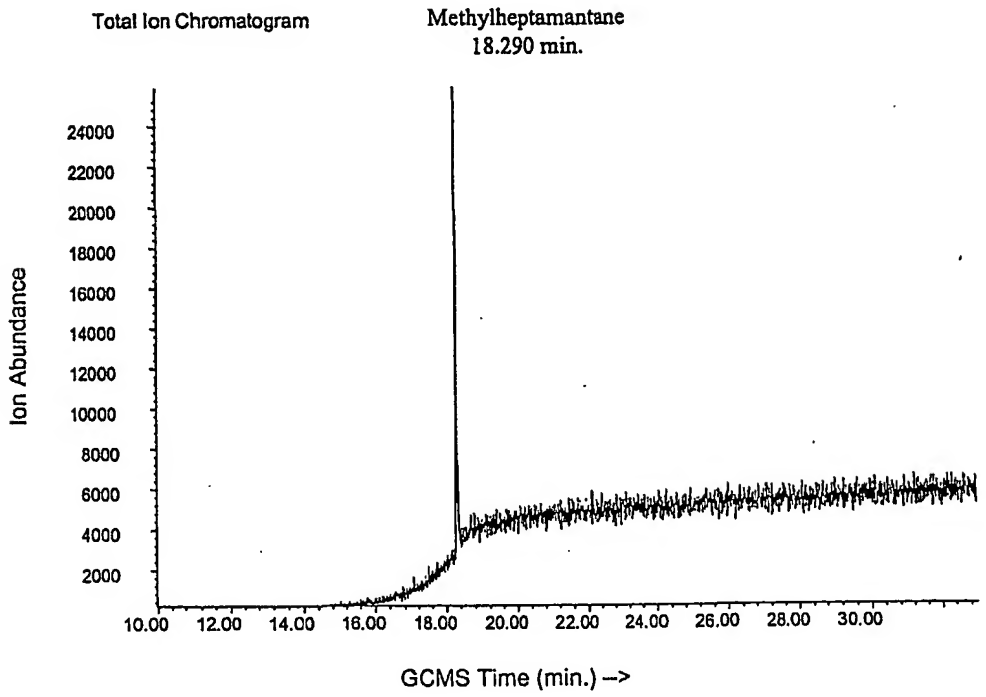

Heptamantane
mol. wt = 420
16.71 min.
M+
420
Ion Abundance
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
210
50
100
150
200
250
300
350
400
m/z-->

FIG. 74

A)


Total Ion Chromatogram
Methylheptamantane
18.290 min.
Ion Abundance
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
28.00
30.00
GCMS Time (min.) -->

B)

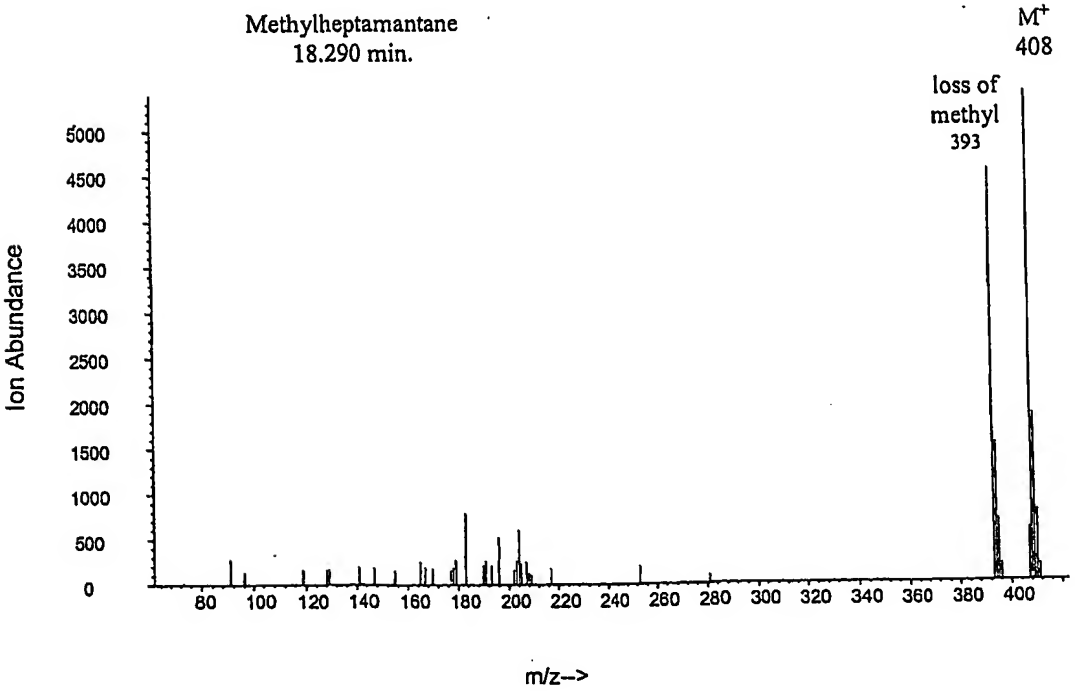
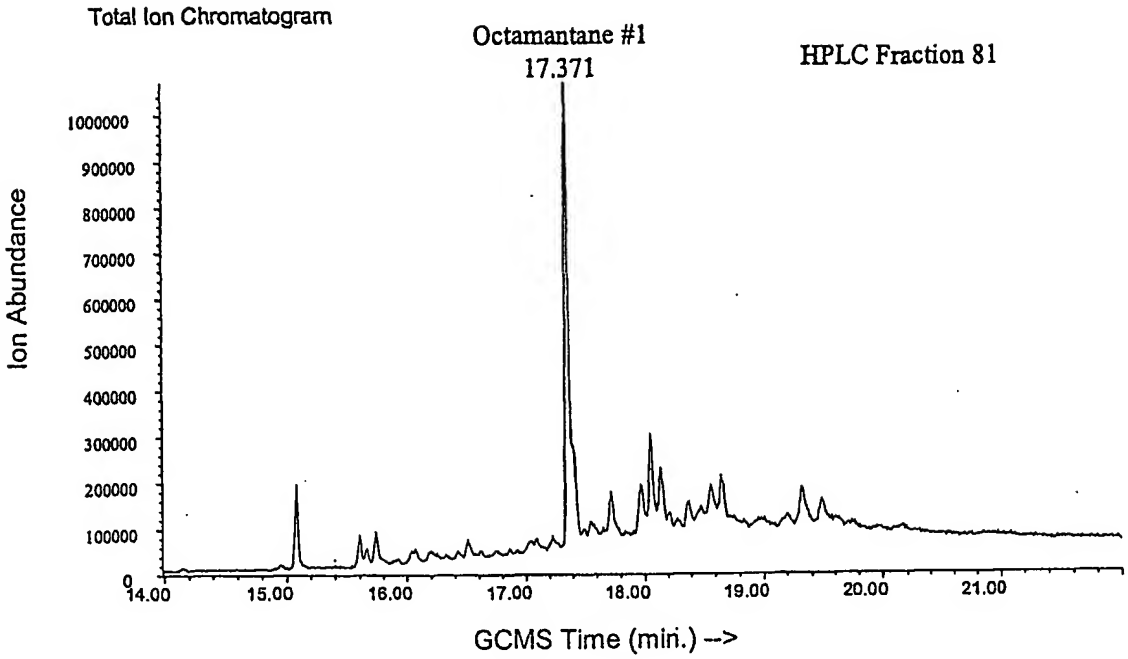

Methylheptamantane
18.290 min.
M+
408
loss of
methyl
393
Ion Abundance
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
m/z-->

FIG. 75

A)


Total Ion Chromatogram
Octamantane #1
17.371
HPLC Fraction 81
Ion Abundance
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
14.00
15.00
16.00
17.00
18.00
19.00
20.00
21.00
GCMS Time (min.) -->

B)

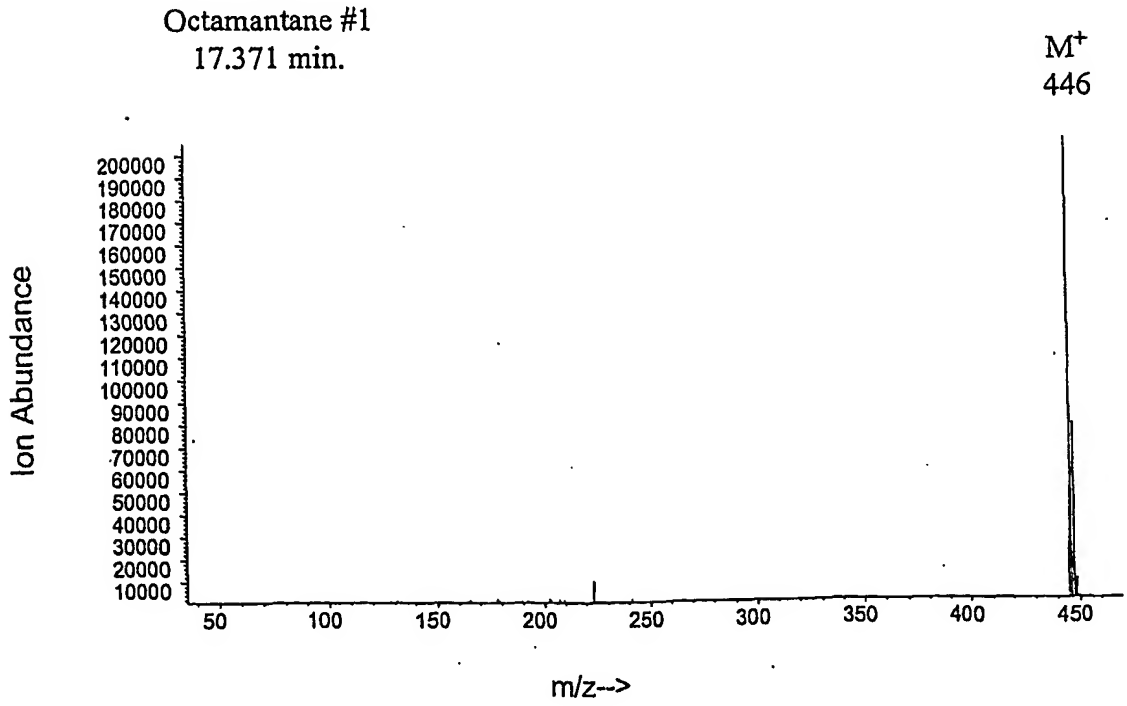

Octamantane #1
17.371 min.
M+
446
Ion Abundance
200000
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
50
100
150
200
250
300
350
400
450
m/z-->

FIG. 76

Octamantane #1
Crystals

FIG. 77

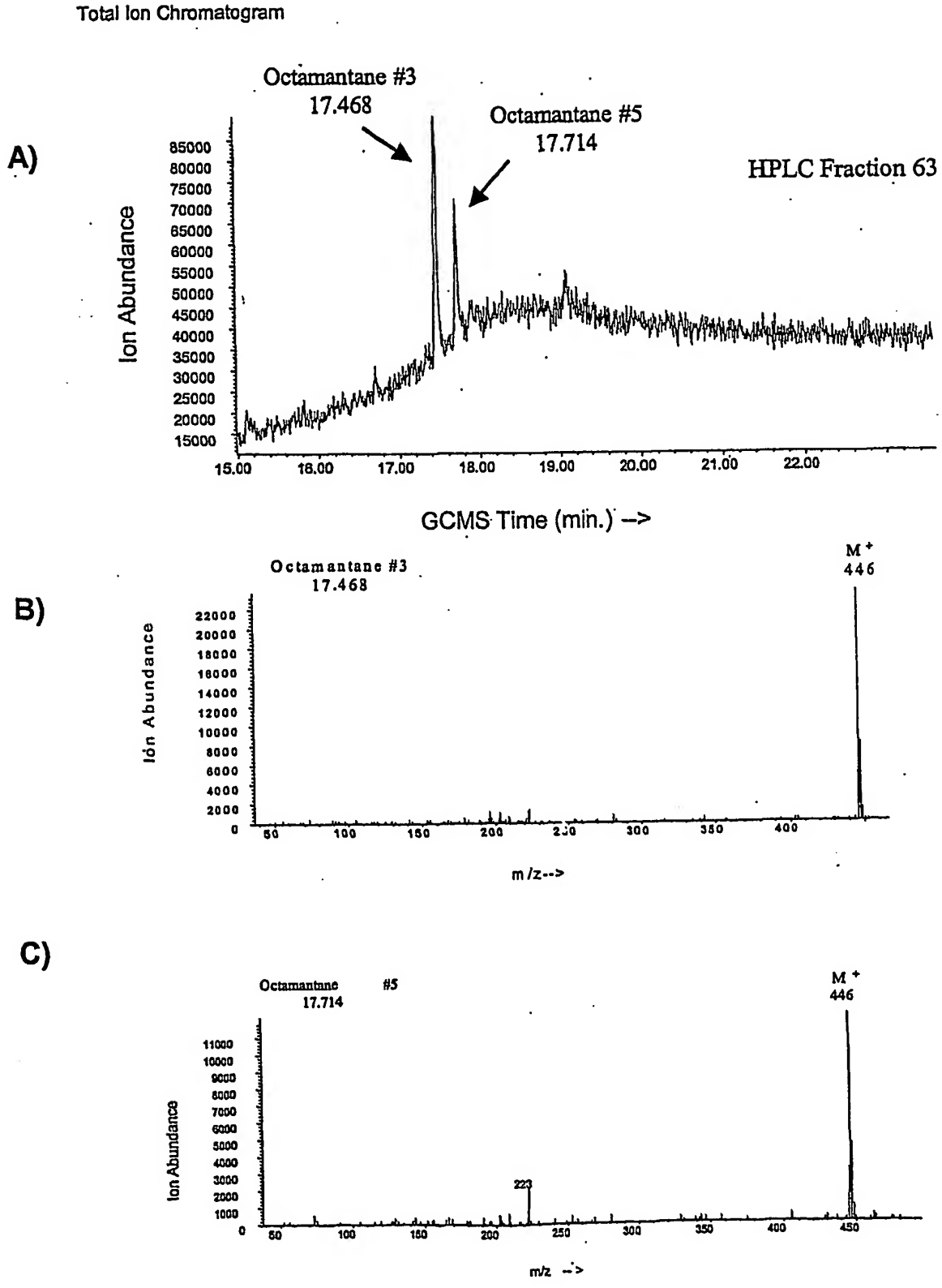
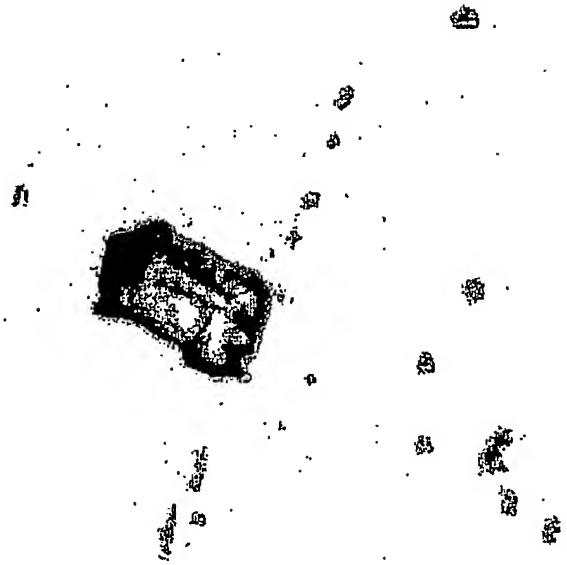

Total Ion Chromatogram
A)
Octamantane #3
17.468
Octamantane #5
17.714
HPLC Fraction 63
Ion Abundance
GCMS Time (min.) -->
B)
Octamantane #3
17.468
M+
446
Ion Abundance
m/z-->
C)
Octamantane #5
17.714
M+
446
223
Ion Abundance
m/z -->

FIG. 78

A)

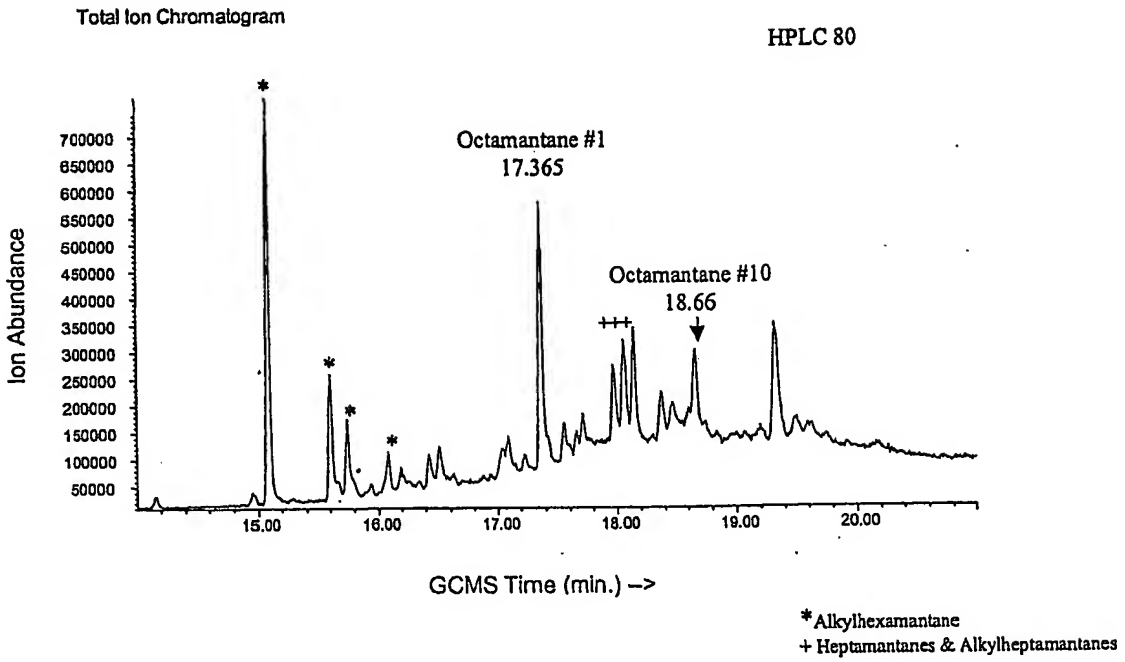


B)

Co-crystal
Octamantane #3 and #5

FIG. 79

A)


Total Ion Chromatogram
HPLC 80
Octamantane #1
17.365
Octamantane #10
18.66
Ion Abundance
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
15.00
16.00
17.00
18.00
19.00
20.00
GCMS Time (min.) -->
*Alkylhexamantane
+ Heptamantanes & Alkylheptamantanes

B)

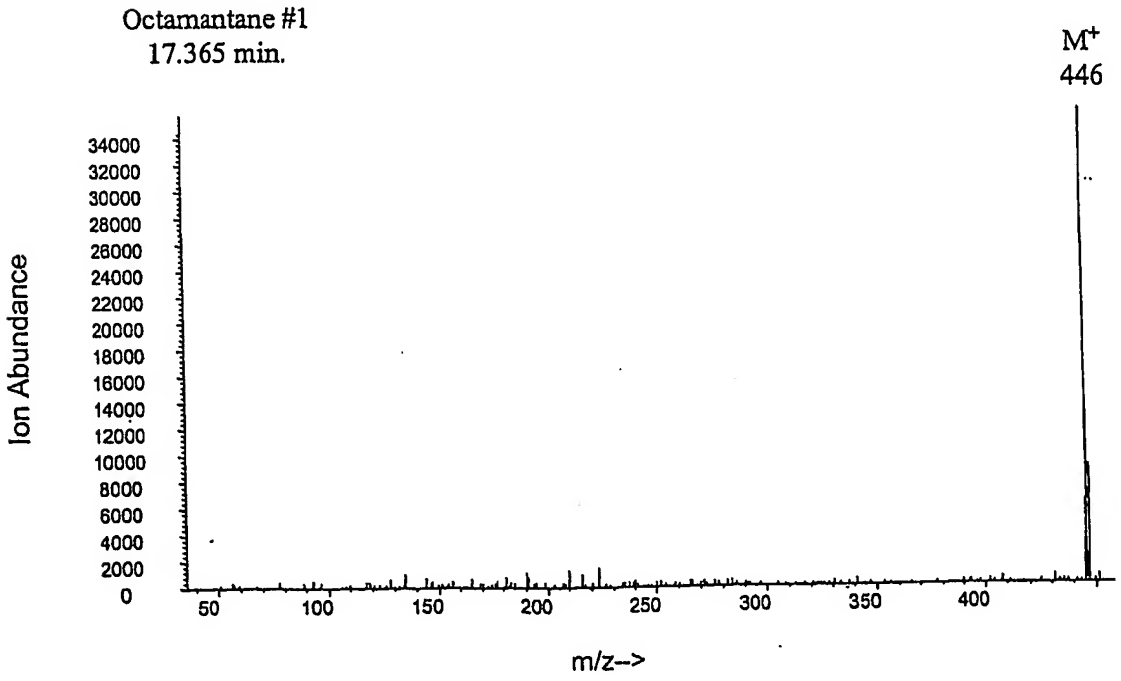

Octamantane #1
17.365 min.
M+
446
Ion Abundance
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
50
100
150
200
250
300
350
400
m/z-->

FIG. 80

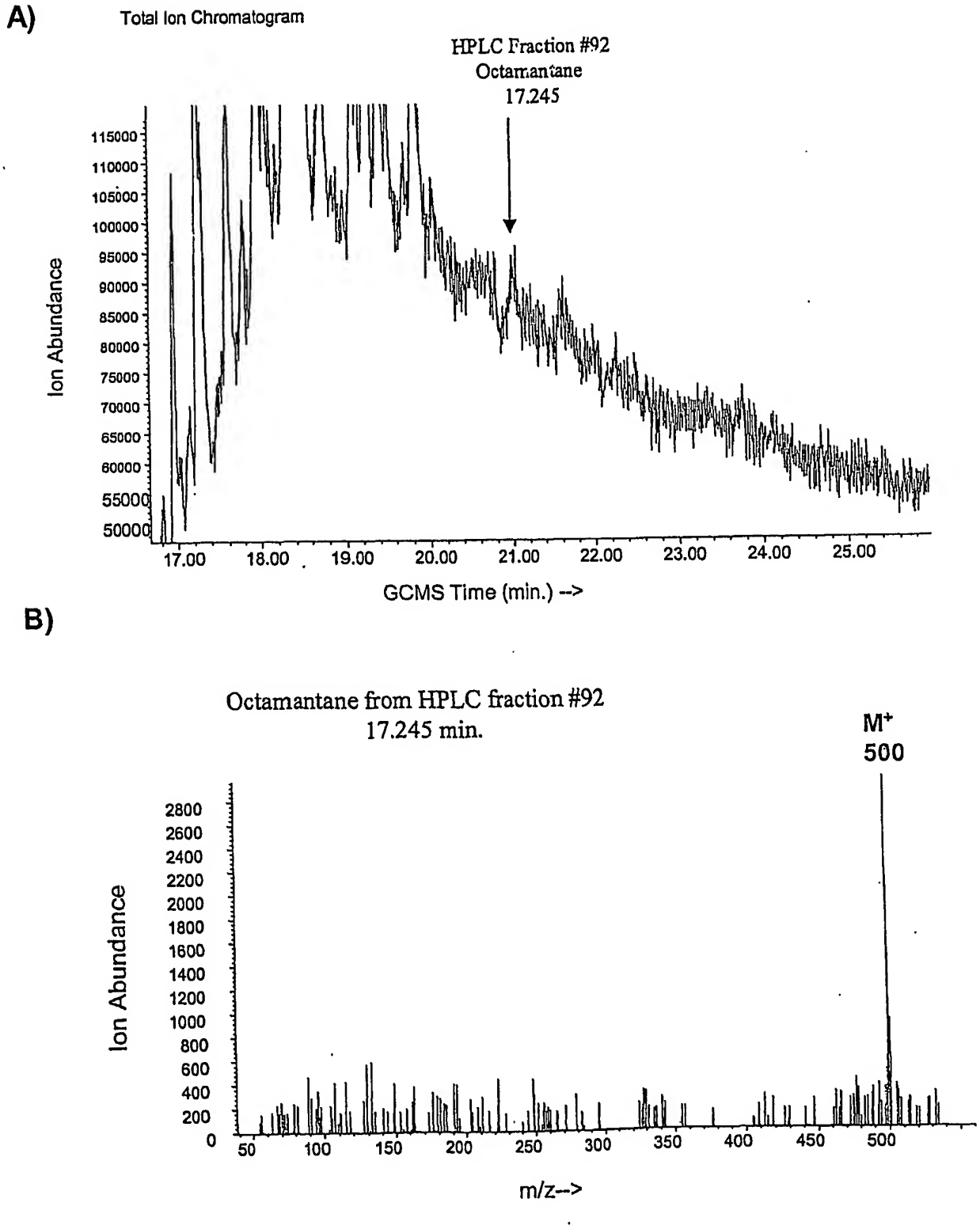
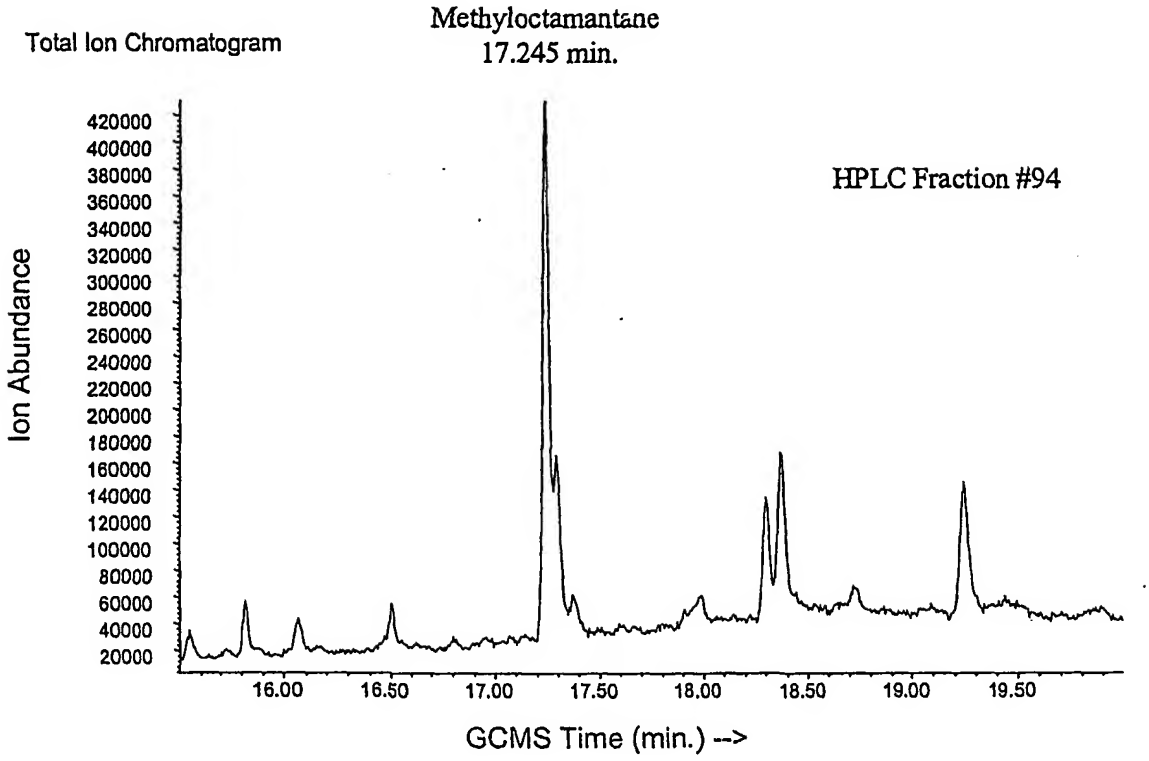

A)
Total Ion Chromatogram
HPLC Fraction #92
Octamantane
17.245
Ion Abundance
115000
110000
105000
100000
95000
90000
85000
80000
75000
70000
65000
60000
55000
50000
17.00
18.00
19.00
20.00
21.00
22.00
23.00
24.00
25.00
GCMS Time (min.) -->
B)
Octamantane from HPLC fraction #92
17.245 min.
M+
500
Ion Abundance
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
50
100
150
200
250
300
350
400
450
500
m/z-->

FIG. 81

A)


Total Ion Chromatogram
Methyloctamantane
17.245 min.
HPLC Fraction #94
Ion Abundance
420000
400000
380000
360000
340000
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
16.00
16.50
17.00
17.50
18.00
18.50
19.00
19.50
GCMS Time (min.) -->

B)

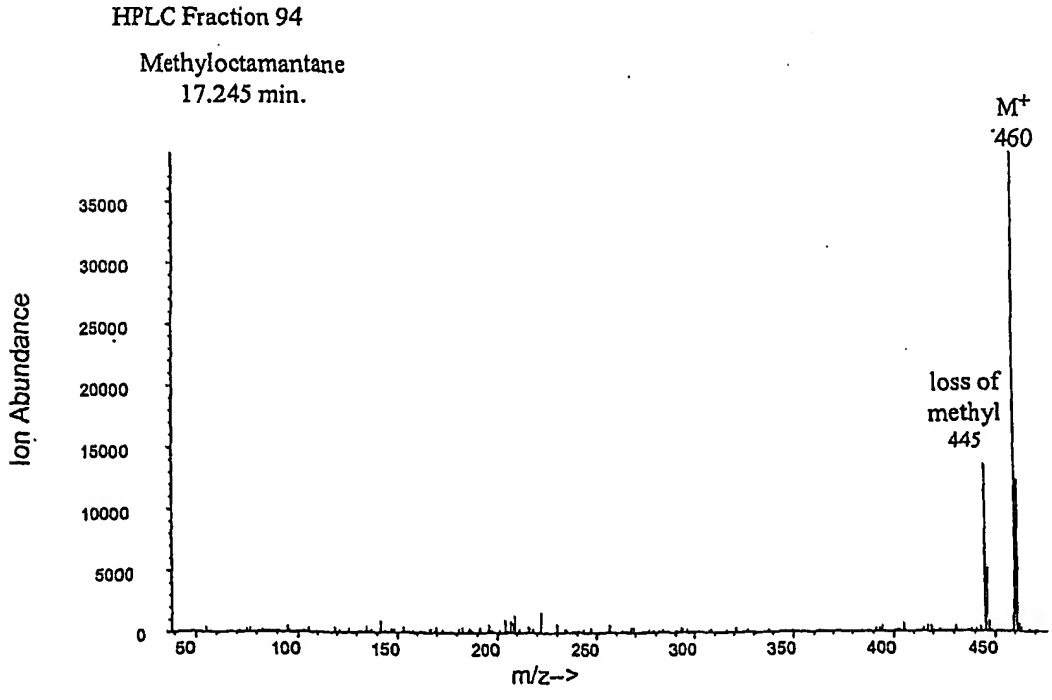

HPLC Fraction 94
Methyloctamantane
17.245 min.
M+
460
loss of
methyl
445
Ion Abundance
35000
30000
25000
20000
15000
10000
5000
0
50
100
150
200
250
300
350
400
450
m/z-->

FIG. 82

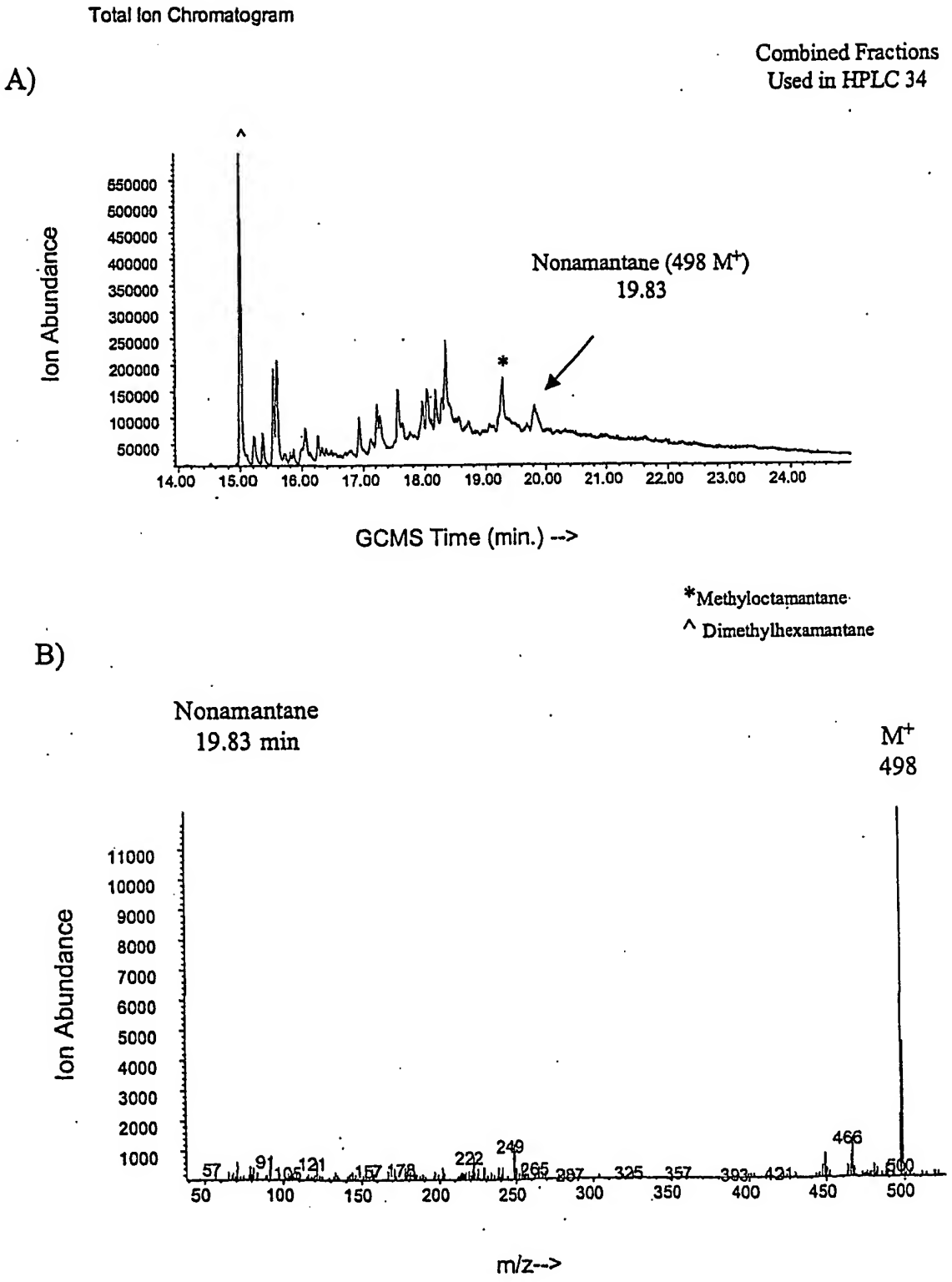
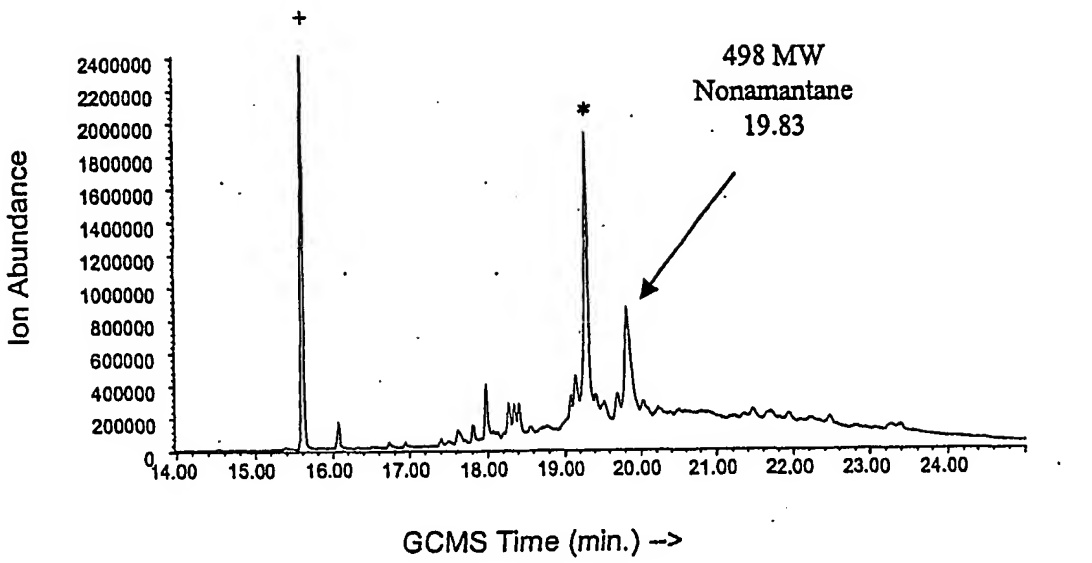

Total Ion Chromatogram
A)
Combined Fractions
Used in HPLC 34
Ion Abundance
650000
600000
450000
400000
350000
300000
250000
200000
150000
100000
50000
14.00
15.00
16.00
17.00
18.00
19.00
20.00
21.00
22.00
23.00
24.00
Nonamantane (498 M+)
19.83
GCMS Time (min.) -->
*Methyloctamantane
^ Dimethylhexamantane
B)
Nonamantane
19.83 min
M+
498
Ion Abundance
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
57
91
105
121
157
178
222
249
265
287
325
357
393
431
466
500
50
100
150
200
250
300
350
400
450
500
m/z-->

FIG. 83

A)



*Alkyloctamantane
+ Diamantane dimer

B)

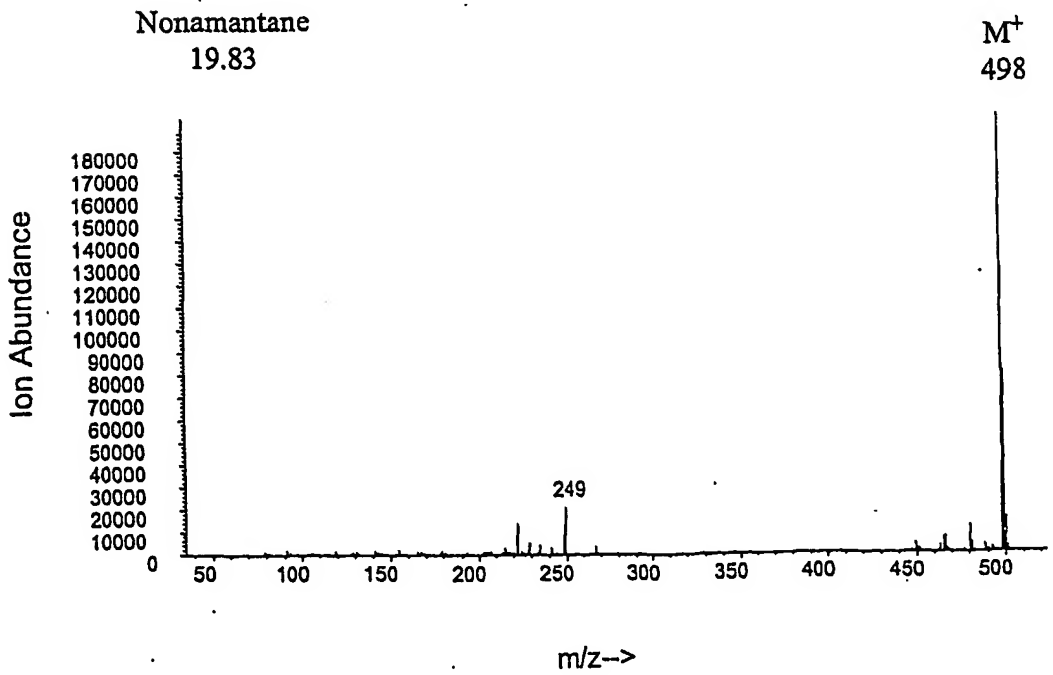


FIG. 84

A)

Crystal of Nonamantane (Mol. Wt. 498)

B)

Mass Spectrum of Dissolved Crystal of Nonamantane
Retention time 19.83 min.

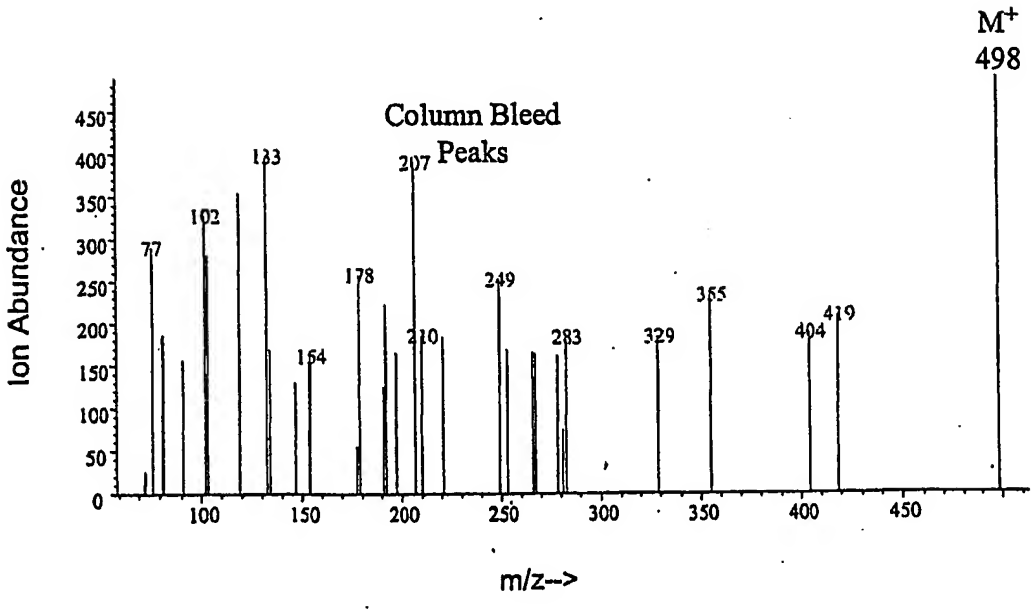
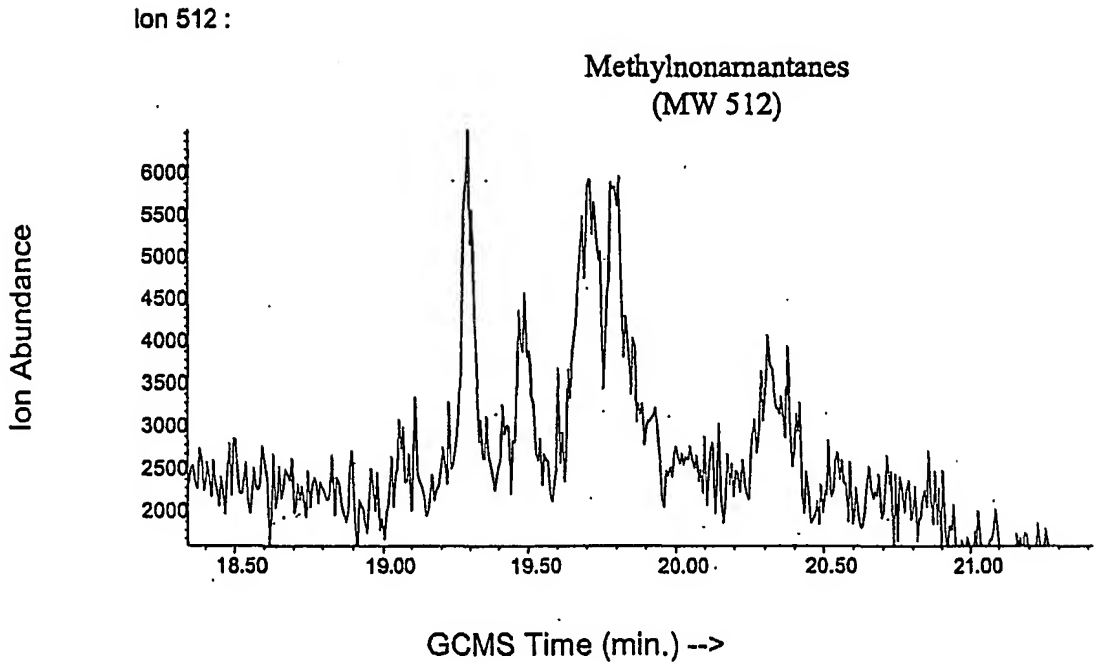


FIG. 85

A)


Ion 512 :
Methylnonamantanes
(MW 512)
Ion Abundance
6000
5500
5000
4500
4000
3500
3000
2500
2000
18.50
19.00
19.50
20.00
20.50
21.00
GCMS Time (min.) -->

B)

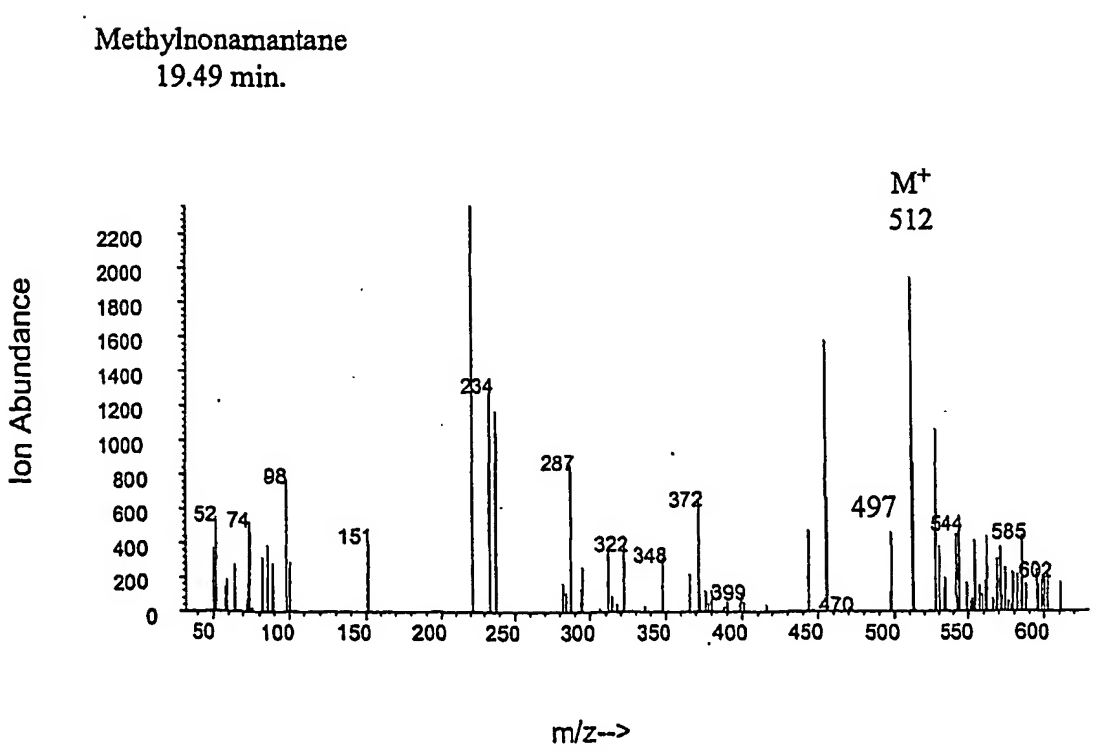
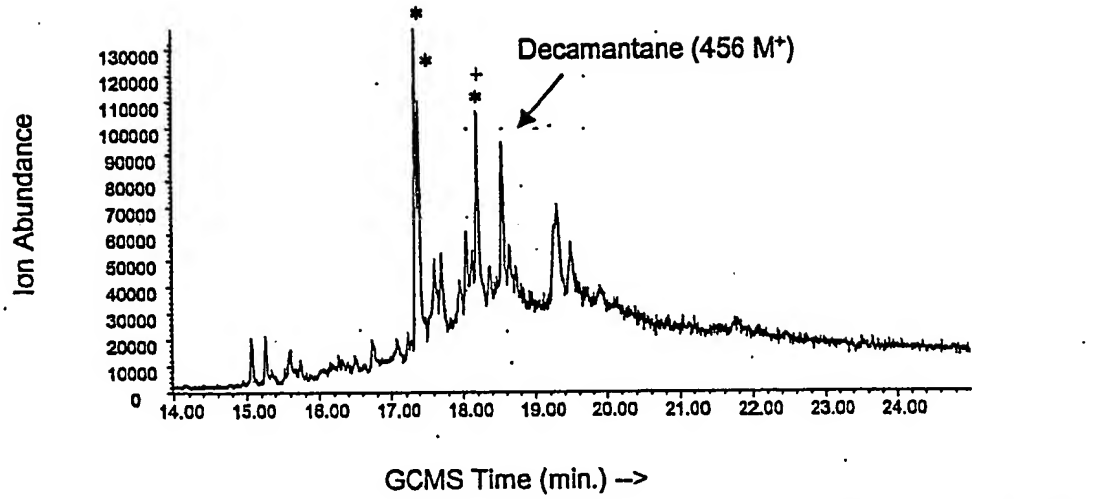

Methylnonamantane
19.49 min.
M+
512
Ion Abundance
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
52
74
98
151
234
287
322
348
372
399
470
497
544
585
602
50
100
150
200
250
300
350
400
450
500
550
600
m/z-->

FIG. 86

A)



*Octamantanes, MW 446
+ Heptamantane, MW 448

B)

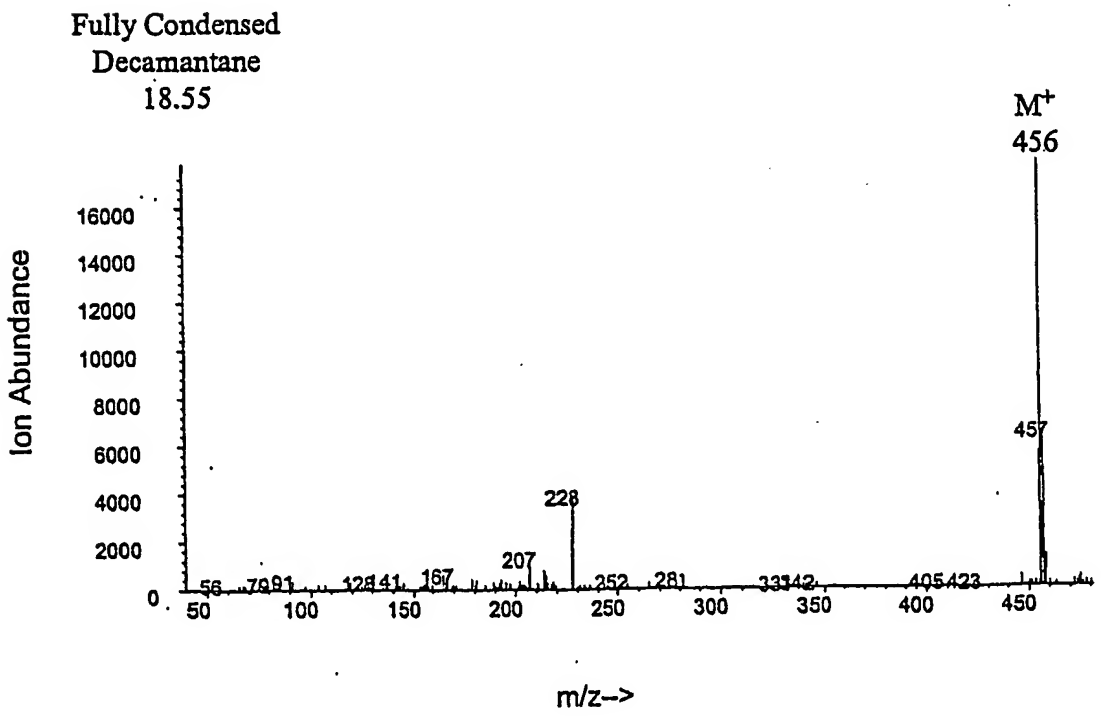


FIG. 87

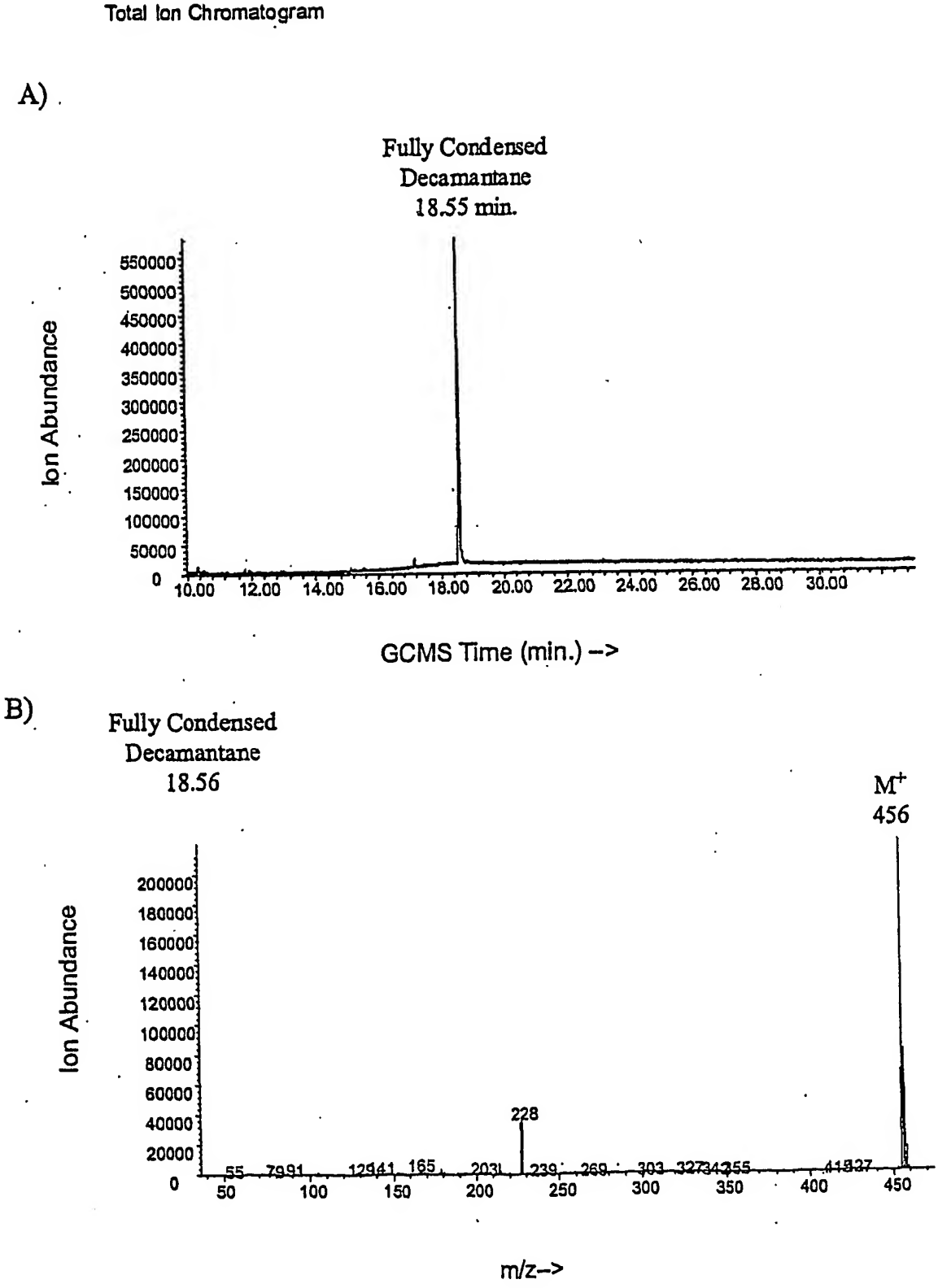

Total Ion Chromatogram
A)
Fully Condensed
Decamantane
18.55 min.
Ion Abundance
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
28.00
30.00
GCMS Time (min.) -->
B)
Fully Condensed
Decamantane
18.56
M+
456
Ion Abundance
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
228
55
79
91
129
141
165
203
239
269
303
327
341
355
418
427
50
100
150
200
250
300
350
400
450
m/z-->

FIG. 88

A)

Crystal of Fully Condensed Decamantane

B) Mass Spectrum of Dissolved Crystal of Fully Comndensed Decamantane
Retention time 18.54 min.

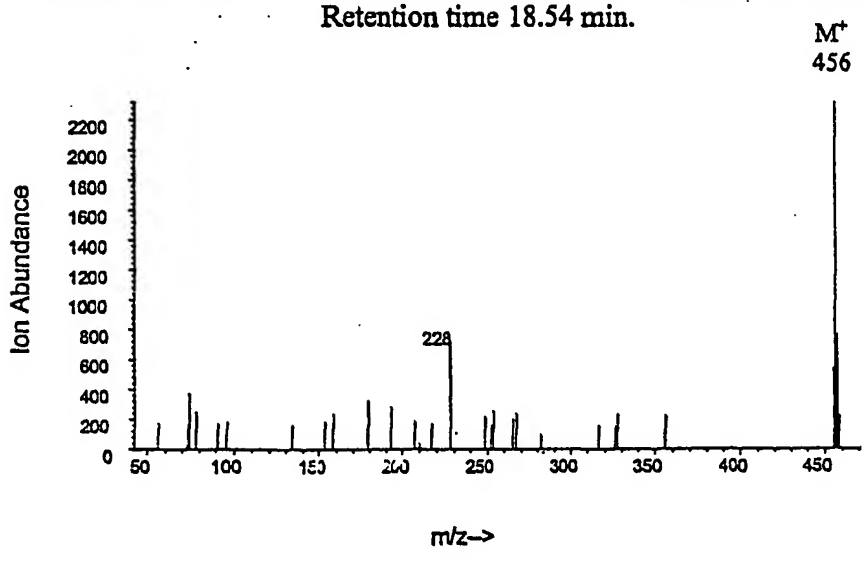
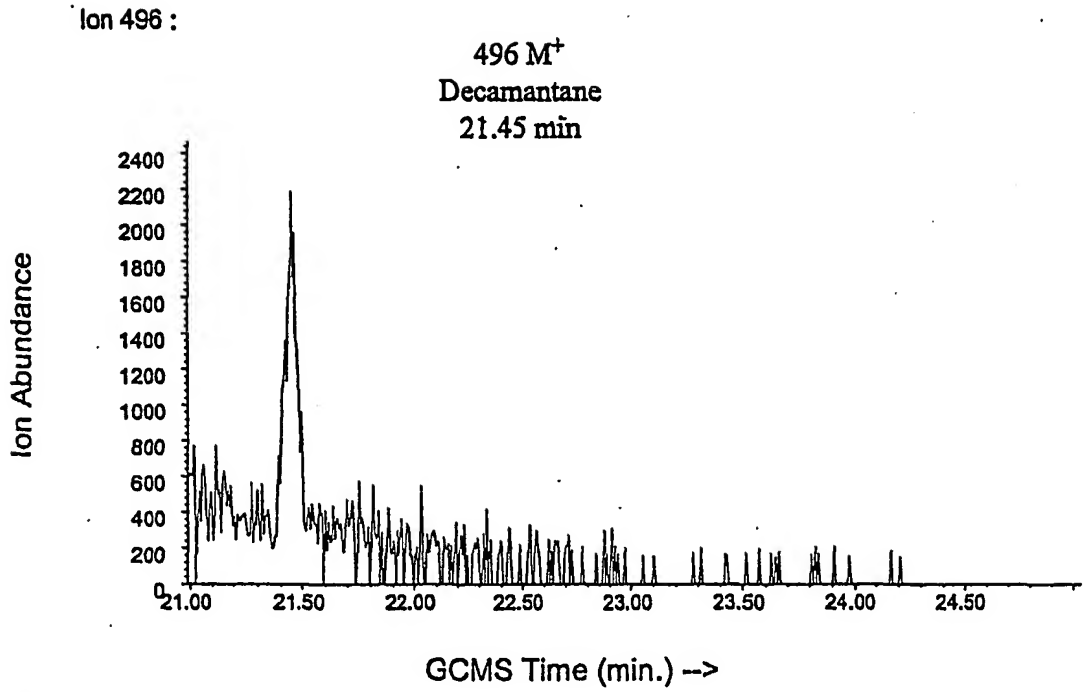


FIG. 89

A)


Ion 496 :
496 M+
Decamantane
21.45 min
Ion Abundance
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
21.00
21.50
22.00
22.50
23.00
23.50
24.00
24.50
GCMS Time (min.) -->

B)

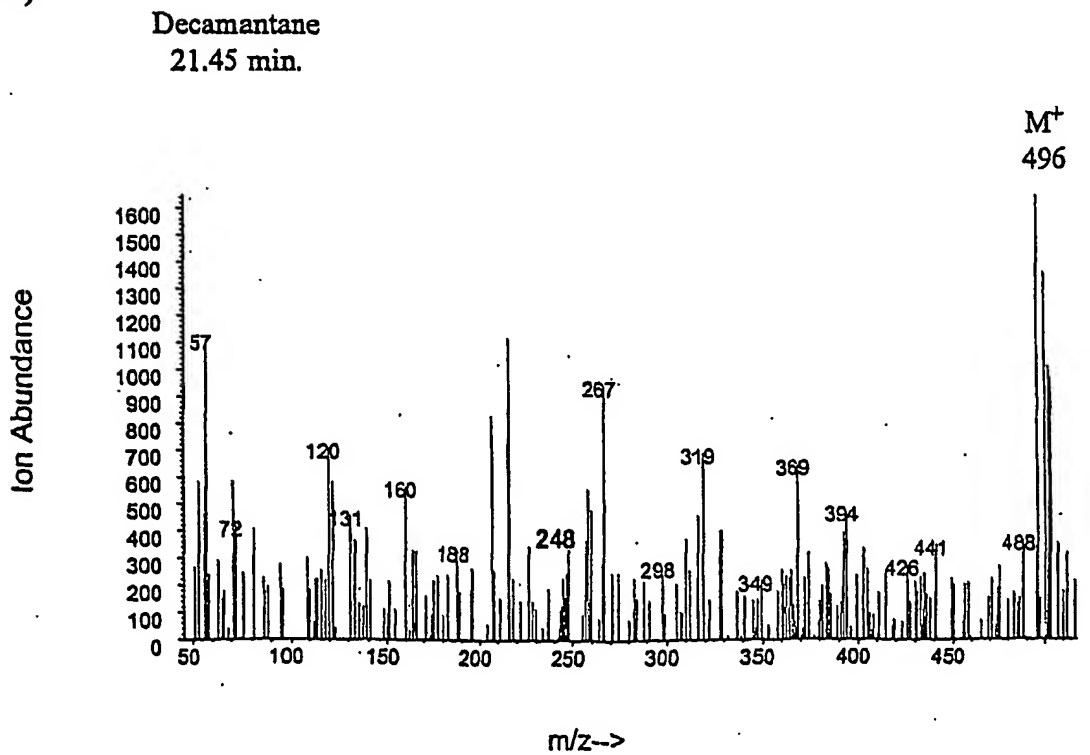
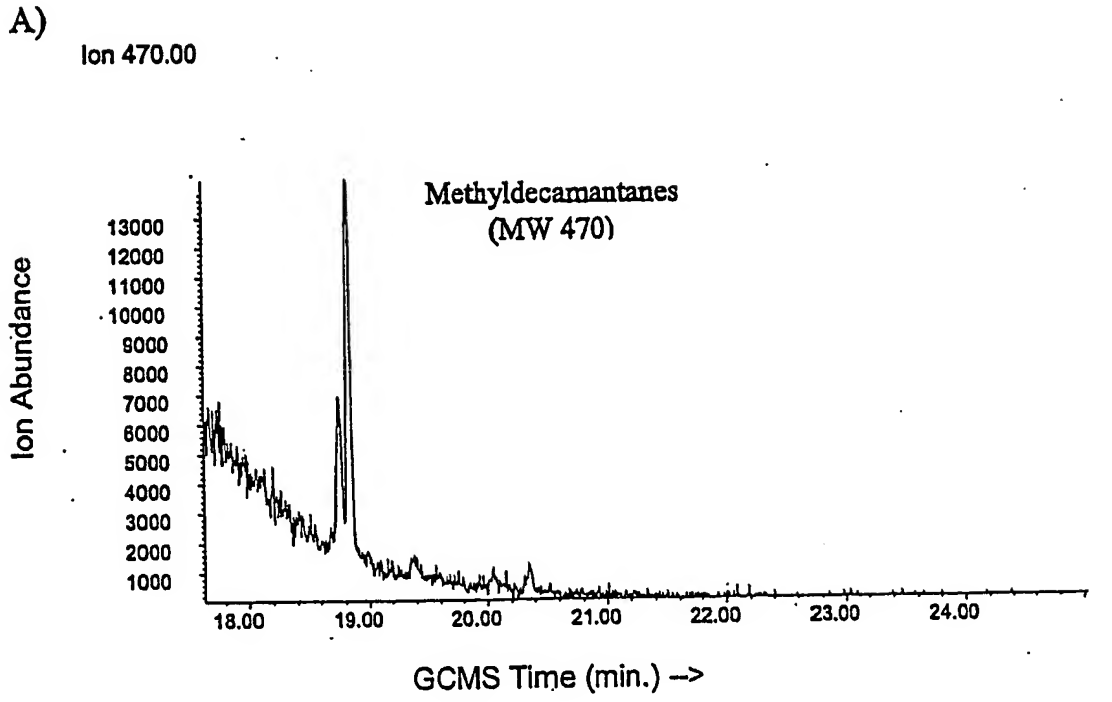

Decamantane
21.45 min.
M+
496
Ion Abundance
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
57
72
120
131
160
188
248
267
298
319
349
369
394
426
441
488
50
100
150
200
250
300
350
400
450
m/z-->

FIG. 90


A)
Ion 470.00
Methyldecamantanes
(MW 470)
Ion Abundance
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
18.00
19.00
20.00
21.00
22.00
23.00
24.00
GCMS Time (min.) -->

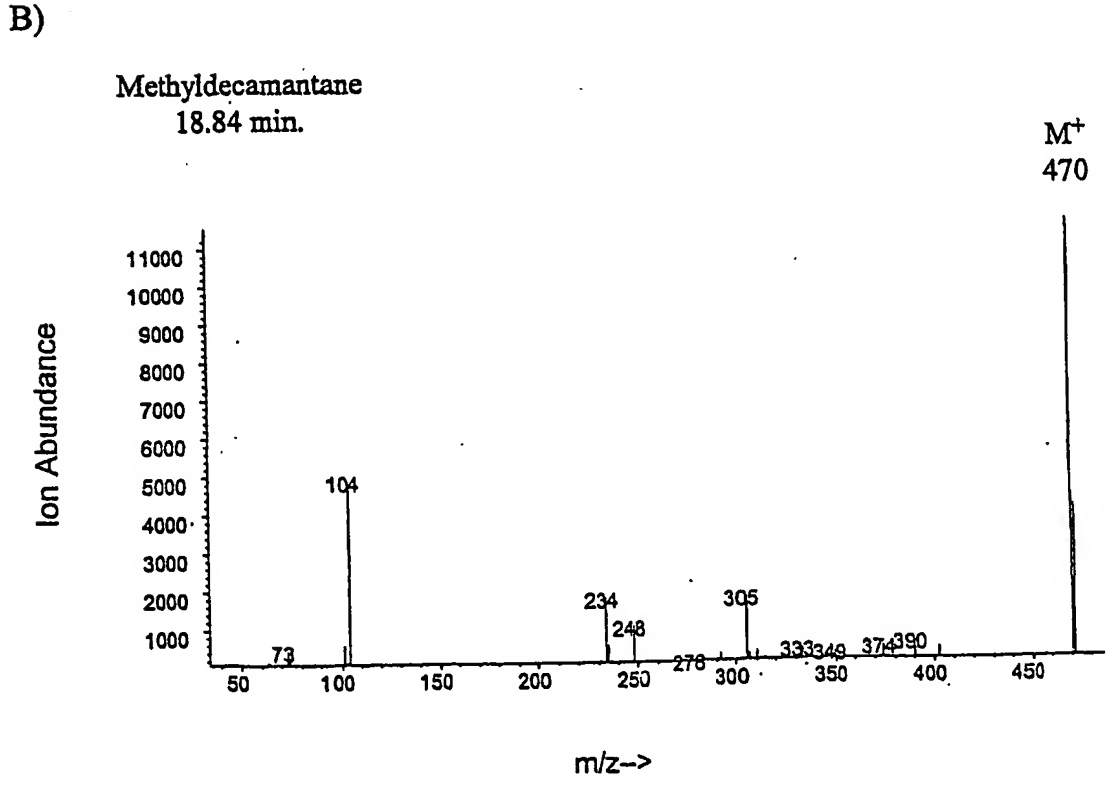
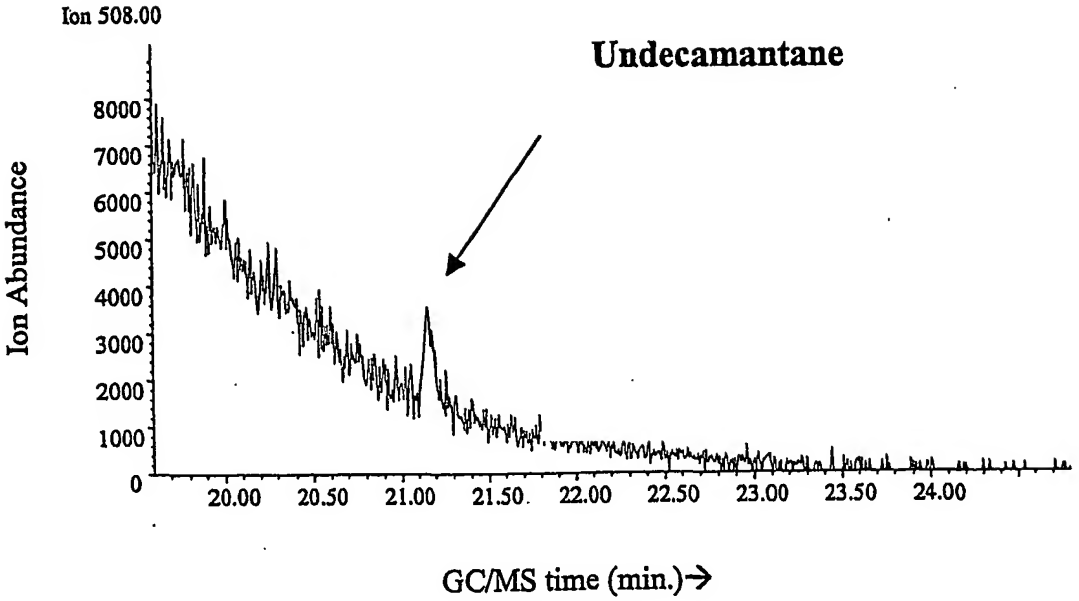

B)
Methyldecamantane
18.84 min.
M+
470
Ion Abundance
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
104
73
234
248
278
305
333
349
374
390
50
100
150
200
250
300
350
400
450
m/z-->

FIG. 91

A)


Ion 508.00
Undecamantane
Ion Abundance
8000
7000
6000
5000
4000
3000
2000
1000
0
20.00
20.50
21.00
21.50
22.00
22.50
23.00
23.50
24.00
GC/MS time (min.)→

B)

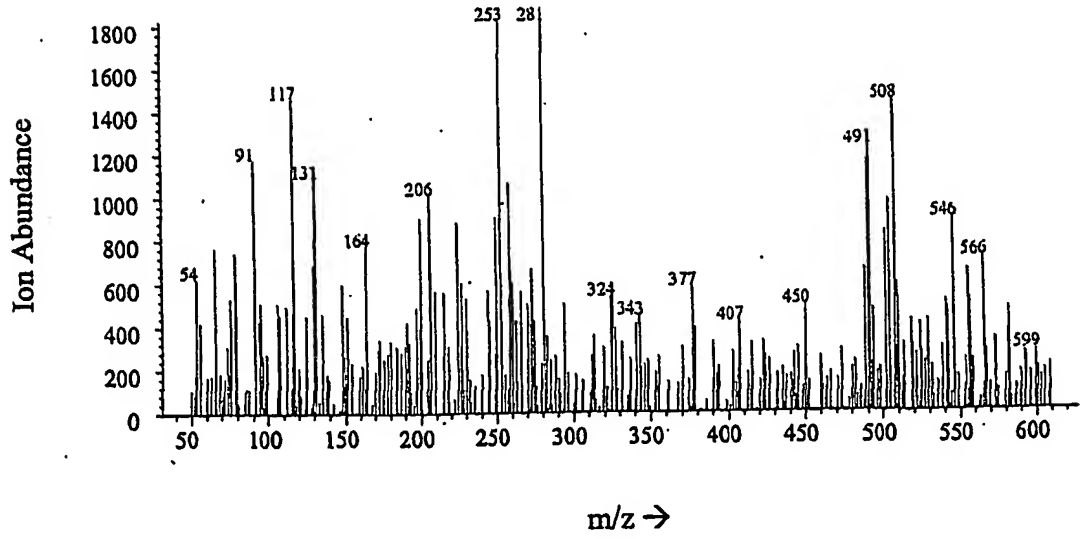
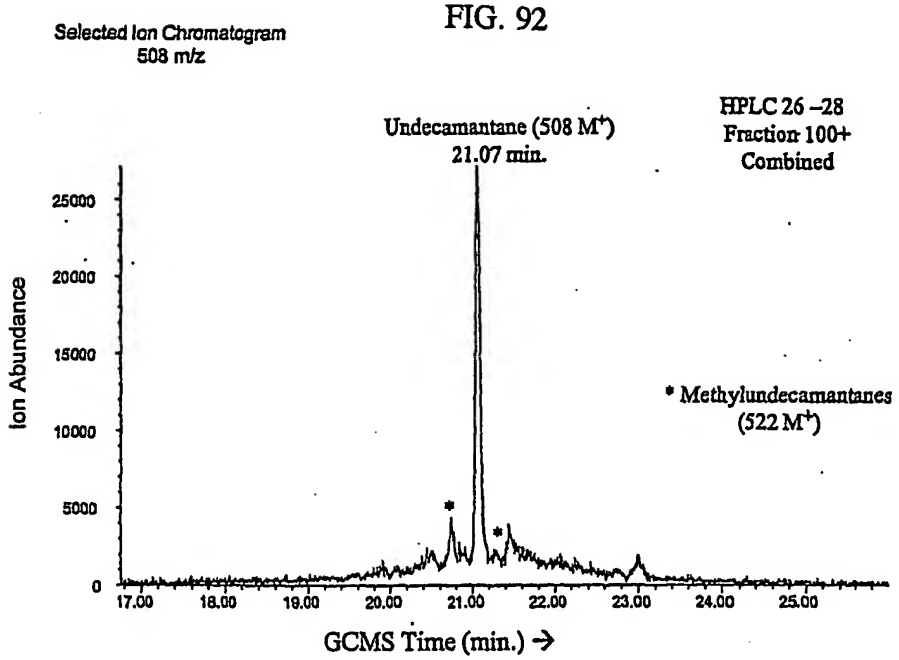
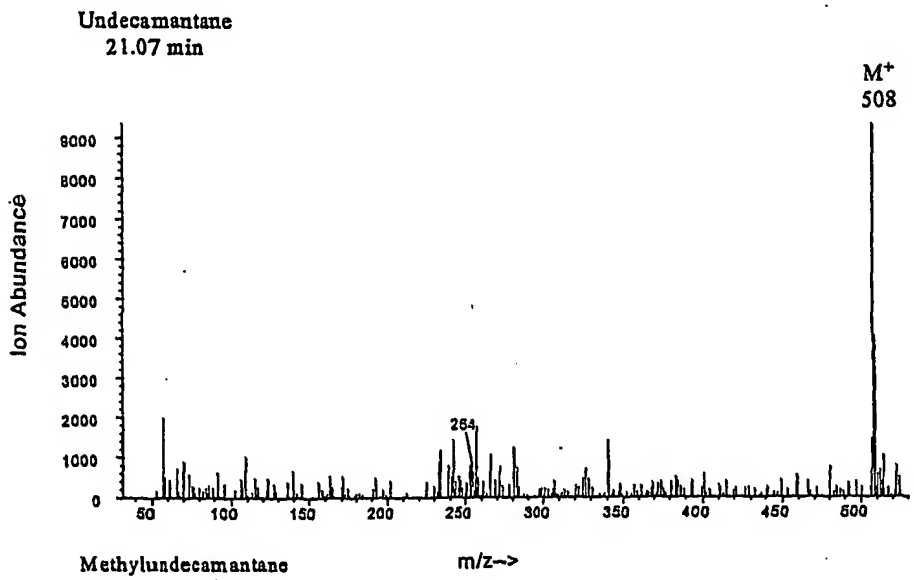

Ion Abundance
1800
1600
1400
1200
1000
800
600
400
200
0
50
100
150
200
250
300
350
400
450
500
550
600
m/z →
54
91
117
131
164
206
253
281
324
343
377
407
450
491
508
546
566
599

FIG. 92

A)


Selected Ion Chromatogram
508 m/z
Undecamantane (508 M+)
21.07 min.
HPLC 26 –28
Fraction 100+
Combined
* Methylundecamantanes
(522 M+)
Ion Abundance
GCMS Time (min.) →

B)


Undecamantane
21.07 min
M+
508
Ion Abundance
264
m/z→

C)

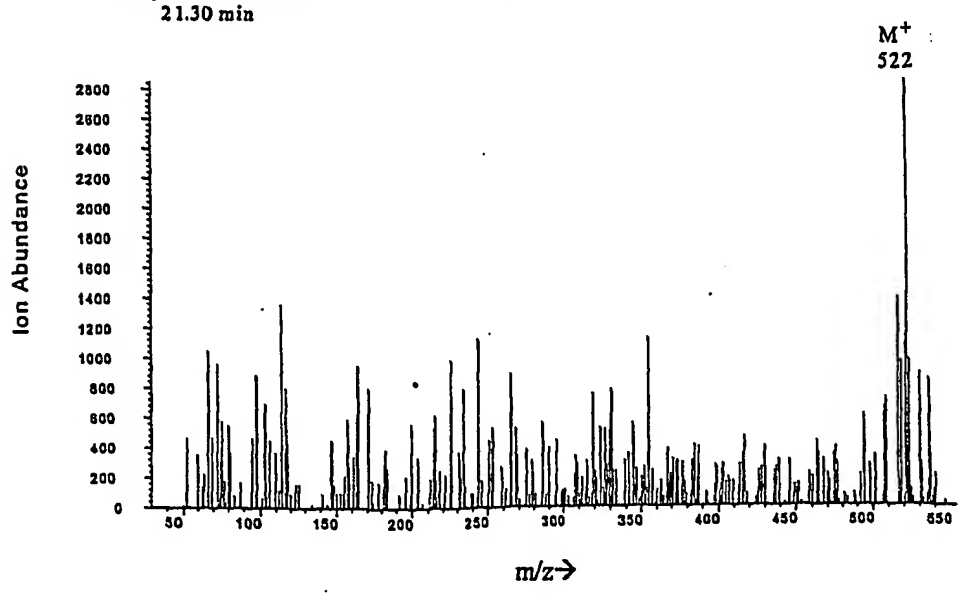

Methylundecamantane
21.30 min
M+
522
Ion Abundance
m/z→

FIG. 93

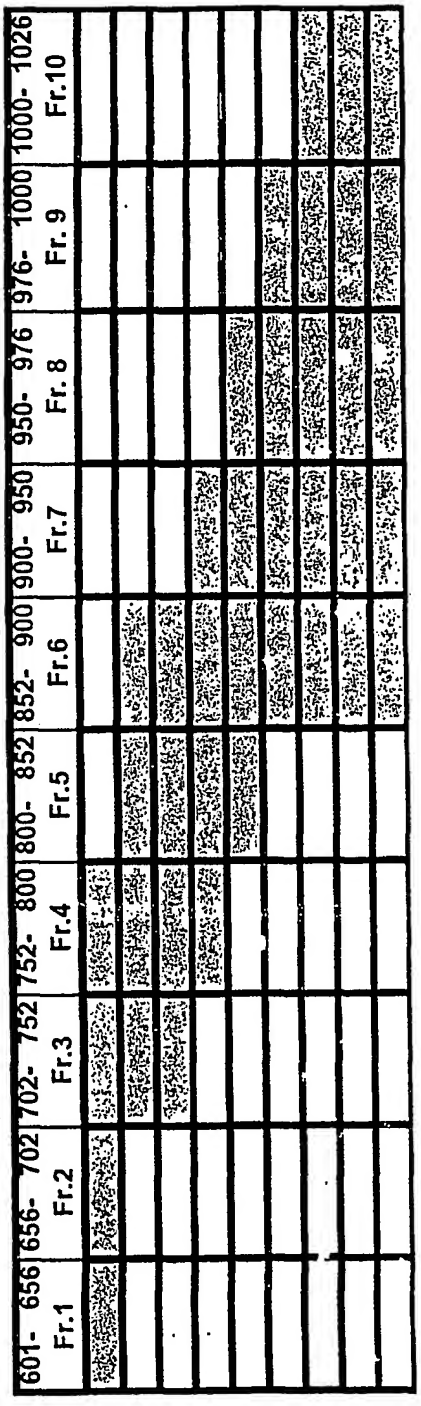
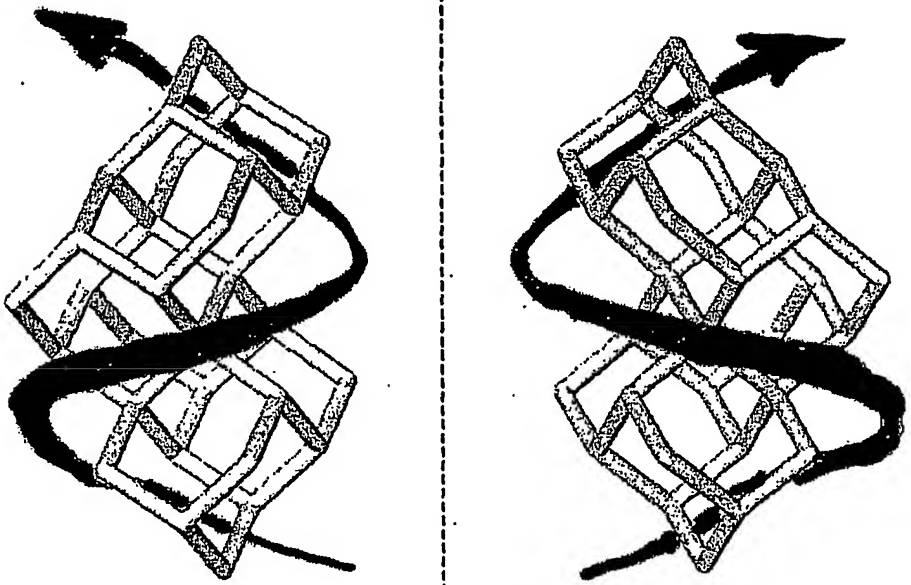

Distillation Cuts Made on Atmospheric Resid of Feedstock B (°C)
601- 656 Fr.1
656- 702 Fr.2
702- 752 Fr.3
752- 800 Fr.4
800- 852 Fr.5
852- 900 Fr.6
900- 950 Fr.7
950- 976 Fr. 8
976- 1000 Fr. 9
1000- 1026 Fr.10
Higher Diamondoid
Tetramantanes
Pentamantanes
Cyclohexamantanes
Hexamantanes
Heptamantanes
Octamantanes
Nonamantanes
Decamantanes
Undecamantanes

FIG. 94

Right and Left-Handed Screw-Shaped Higher Diamondoid



Mirror Plane

[12341] A

[12341] B

Right-handed helix
P configuration

Left-handed helix
M configuration

Non-superimposable mirror images, an optically active, helical-shaped Hexamantane

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C13/64

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, PAJ, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 06019 A (MOBIL OIL CORP) 2 March 1995 (1995-03-02) figure 1 see claim 5 (j)	1-45
X	US 5 306 851 A (WU MARGARET M ET AL) 26 April 1994 (1994-04-26) see the table on col. 7 "iso-tetramantane"	1,3

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
5 June 2002	11/06/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Goetz, G

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9506019 A	02-03-1995	US 5414189 A	09-05-1995
		AU 678853 B2	12-06-1997
		AU 7635494 A	21-03-1995
		EP 0715612 A1	12-06-1996
		JP 9501696 T	18-02-1997
		WO 9506019 A1	02-03-1995
US 5306851 A	26-04-1994	NONE	